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The reduction of fluxed and non-fluxed manganese ores by ferromanganese-silicide

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5. RESULTS

5.1. Non-Fluxed Reactions

Experiments were carried out to examine the effect on the manganese recovery with time on the initial temperature as measured by the control thermocouple for temperatures of 1450°, 1500°, 1550° and 1600°C. Figure 35 shows that the initial temperature had little effect on manganese recoveries and the reduction reaction appeared virtually complete within a few minutes from the start of the reaction. The ratio of plant alloy to non-fluxed ore was chosen as 1 to 2 because this ratio approximates that used industrially. A ratio of 6,7 to 10 would be required to supply the stoichiometric amount of silicon in the 22,46 per cent Si ferromanganese-silicide required to reduce all the manganese and iron oxides to the metallic state.

There were no marked increases in manganese recovery from the slag to the alloy phase with increasing temperature. This was probably due to the exothermic reaction giving the initial temperature increase discussed in Section 4.6. which made it difficult to distinguish between the effect of variations in initial furnace temperature as measured by the control thermocouple. Thus the initial temperature of the control thermocouple was held constant at 1500°C and all subsequent experiments were performed at this temperature.

Figure 36 compares manganese recoveries and final alloy silicon contents for the standard reaction time of 15 minutes when both stoichiometric and standard silicon additions are used in the form of plant alloy.

5.2. Fluxed Reactions

The use of lime or magnesia as fluxing additives has been shown to increase the activity of MnO in a manganese - bearing slag. In plant operations, about 20 mass per cent of lime is added to the manganese ore and for a particular alloy - to - ore ratio, the use of fluxes gives

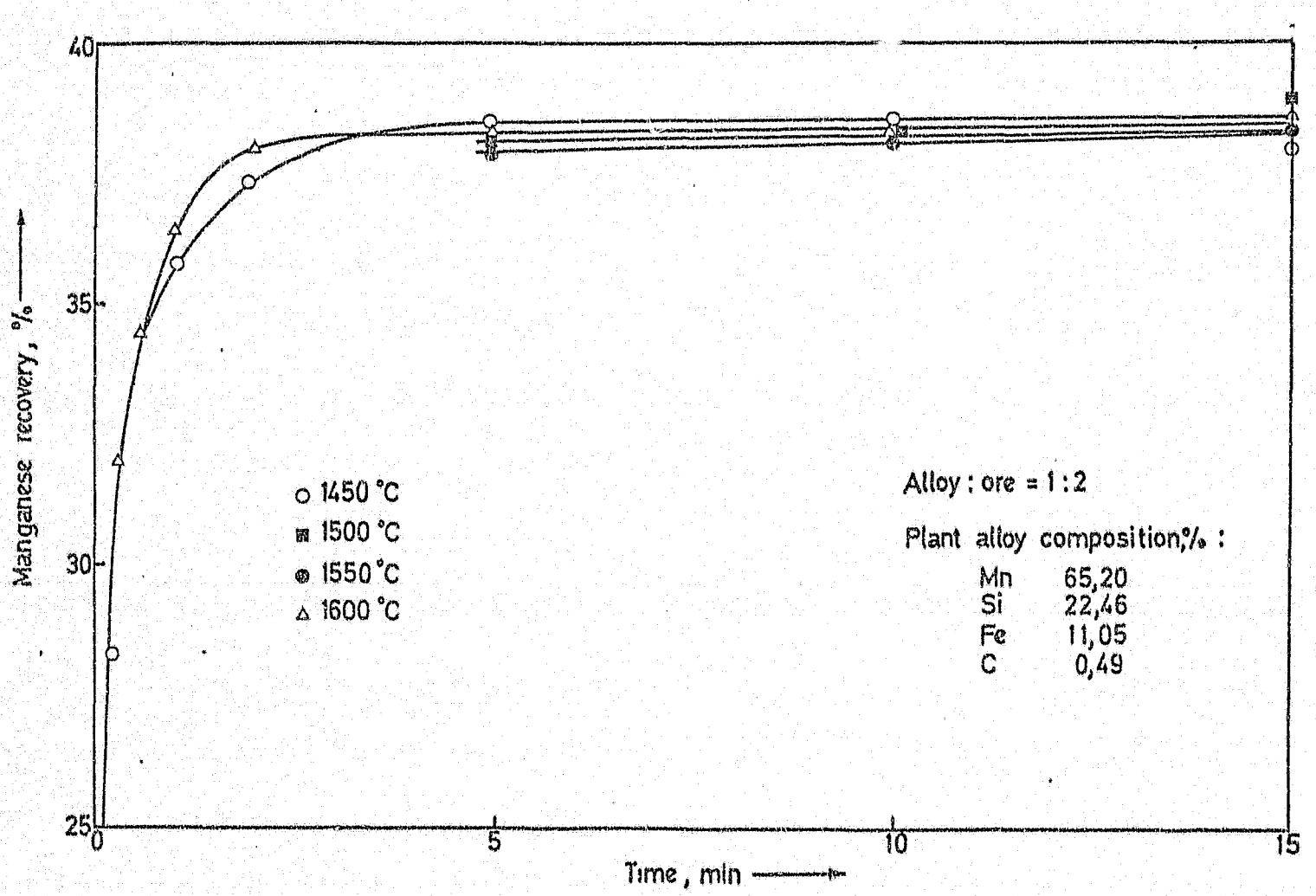


Figure 35 Manganese recovery with time for various initial reaction temperatures.

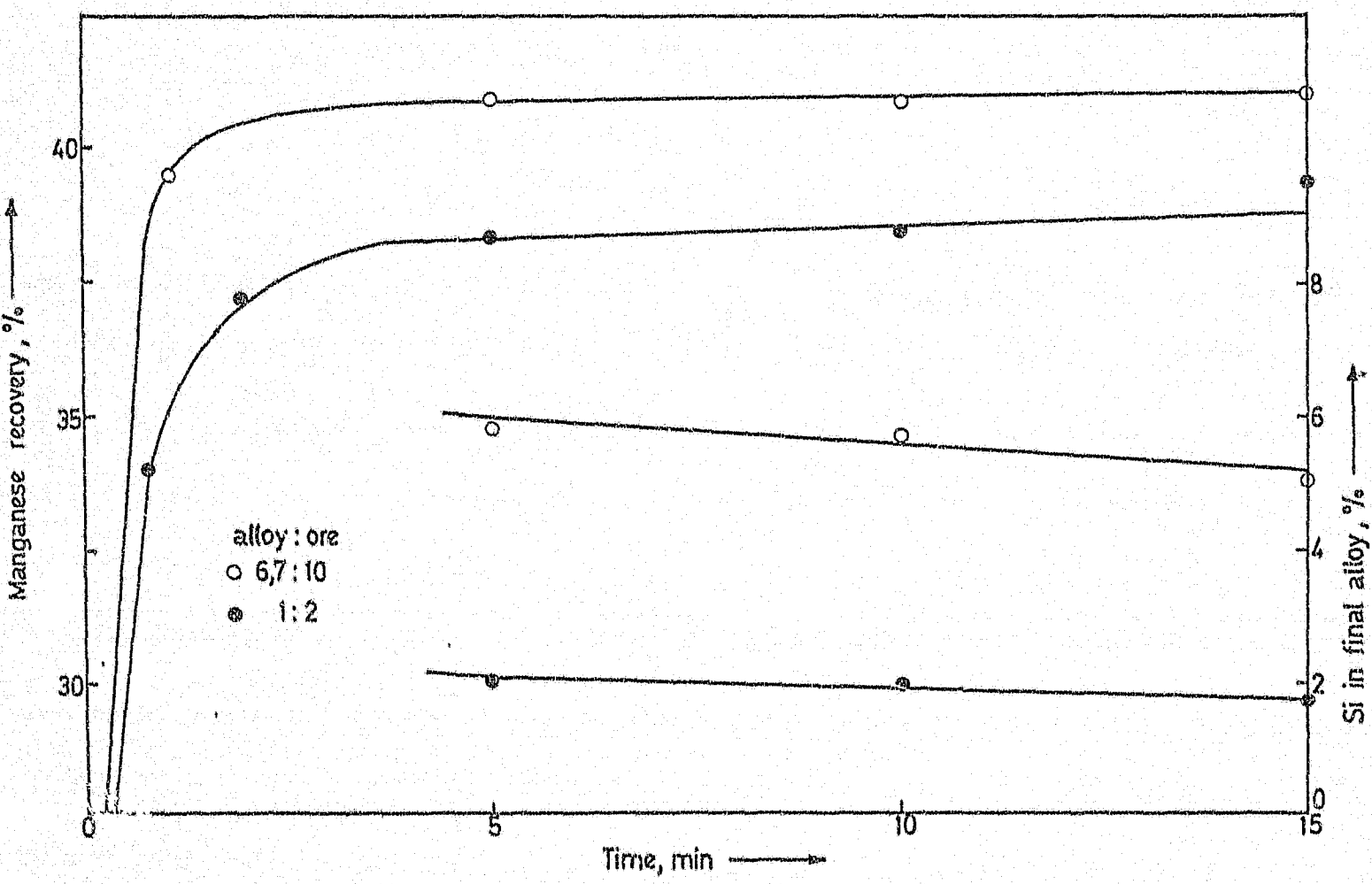


Figure 36. Effects of variations in the alloy:ore ratio on the change in manganese recovery with time at 1500°C.

greater manganese recoveries and lower silicon levels in the final alloyas shown in Figure 37.

A comparison of manganese recoveries for the non-fluxed reduction and the reduction for stagewise lime additions is shown in Figure 38 for reactions using stoichiometric amounts of plant silicide. An increase in manganese recovery of about 5 mass per cent is noted after 5minutes when 20 mass per cent CaO is introduced to the system. No further significant increase in recovery is shown beyond this time and the reduction reaction appeared to be substantially complete after 15 minutes.

Reaction times of 15 minutes were chosen for subsequent experiments but during these small scale experiments with stagewise lime additions, temperature control of the reacting melt was difficult due to the introduction of a relative large mass of cold lime. This led to lower melt temperatures and lower manganese recoveries when compared to the lime - ore premelt practice.

CaO additions were varied at differing alloy - to - ore ratios to establish the extent of manganese reduction from slags contacted with different alloys and containing different amounts of flux. These results are shown in Figure 39 In the high alloy - to - ore ratio reactions, as the lime addition is increased, there is a corresponding increase in manganese recovery. However with low alloy - to - ore ratios, as the lime addition increases the manganese recovery passes through a maximum. In all of these reactions there is a decrease in final alloy silicon concentration with increasing CaO content of the slag.

Experimental work on the effect of replacing CaO by MgO was carried out to determine the effect of partial or total replacement of CaO by calcined dolomite. Fluxing of the reduction reaction by the use of MgO alone was also considered.

Two values of recovery are shown in Figure 40 but for the addition of more than 20 mass per cent MgO, it was not possible to melt the Mamatwan ore - MgO mix even at a temperature of 1550^{o}C. These two recovery values do indicate that the effect of increasing

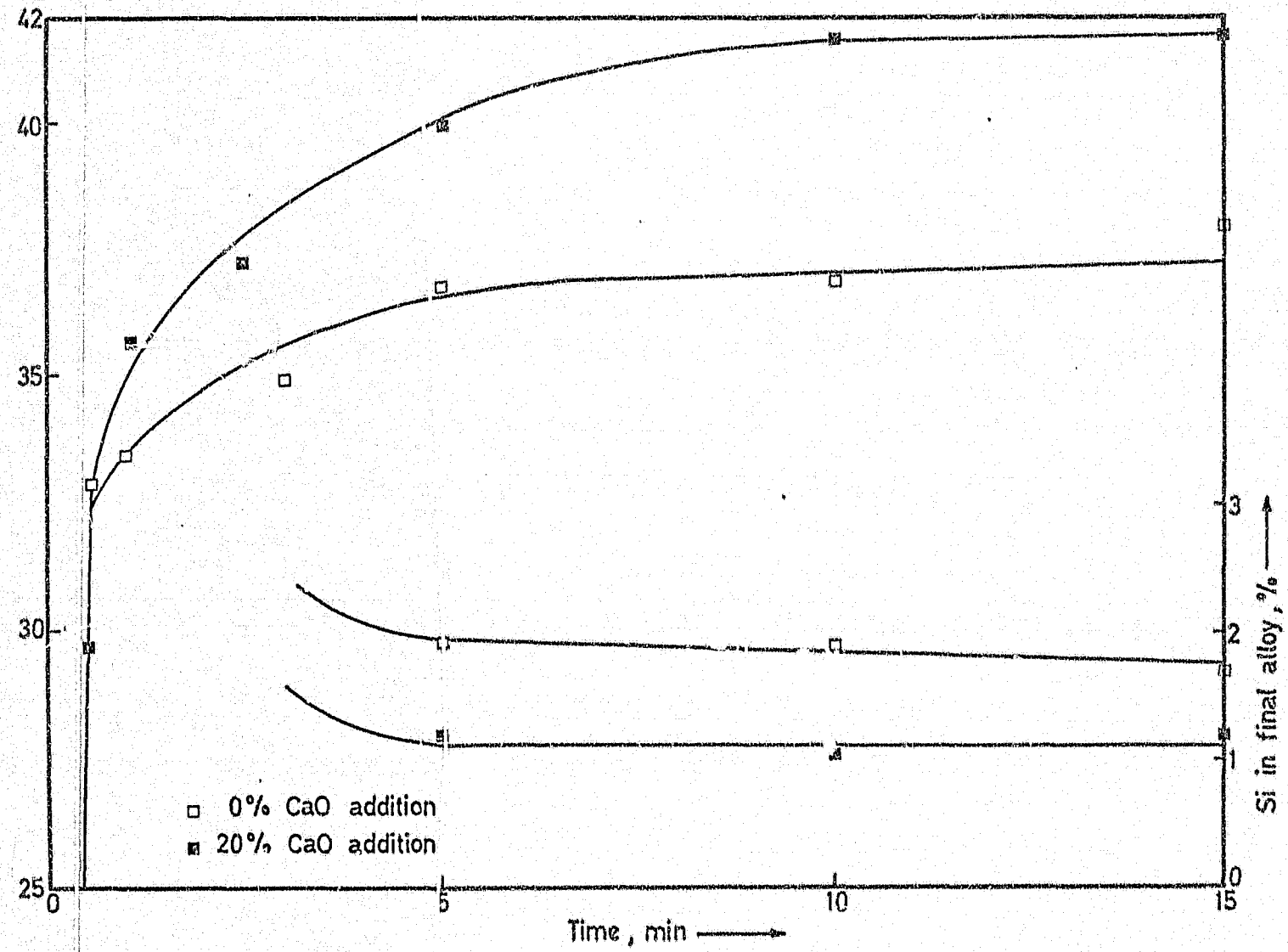


Figure 37. Reactions at 1500°C for a plant alloy-to-ore ratio of 1 to 2

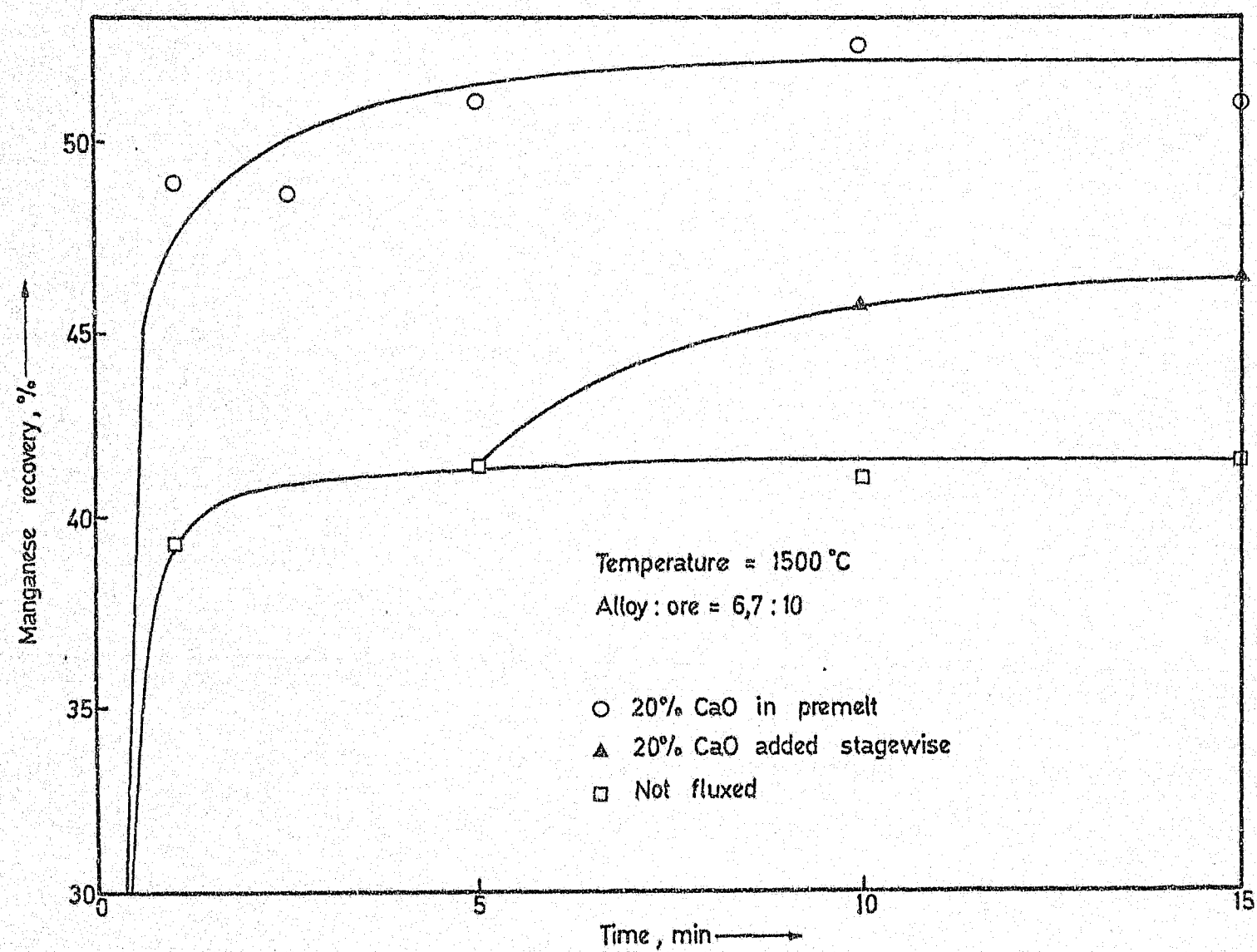


Figure 38. Variation of manganese recovery with time using a stoichiometric amount of FeMnSi.

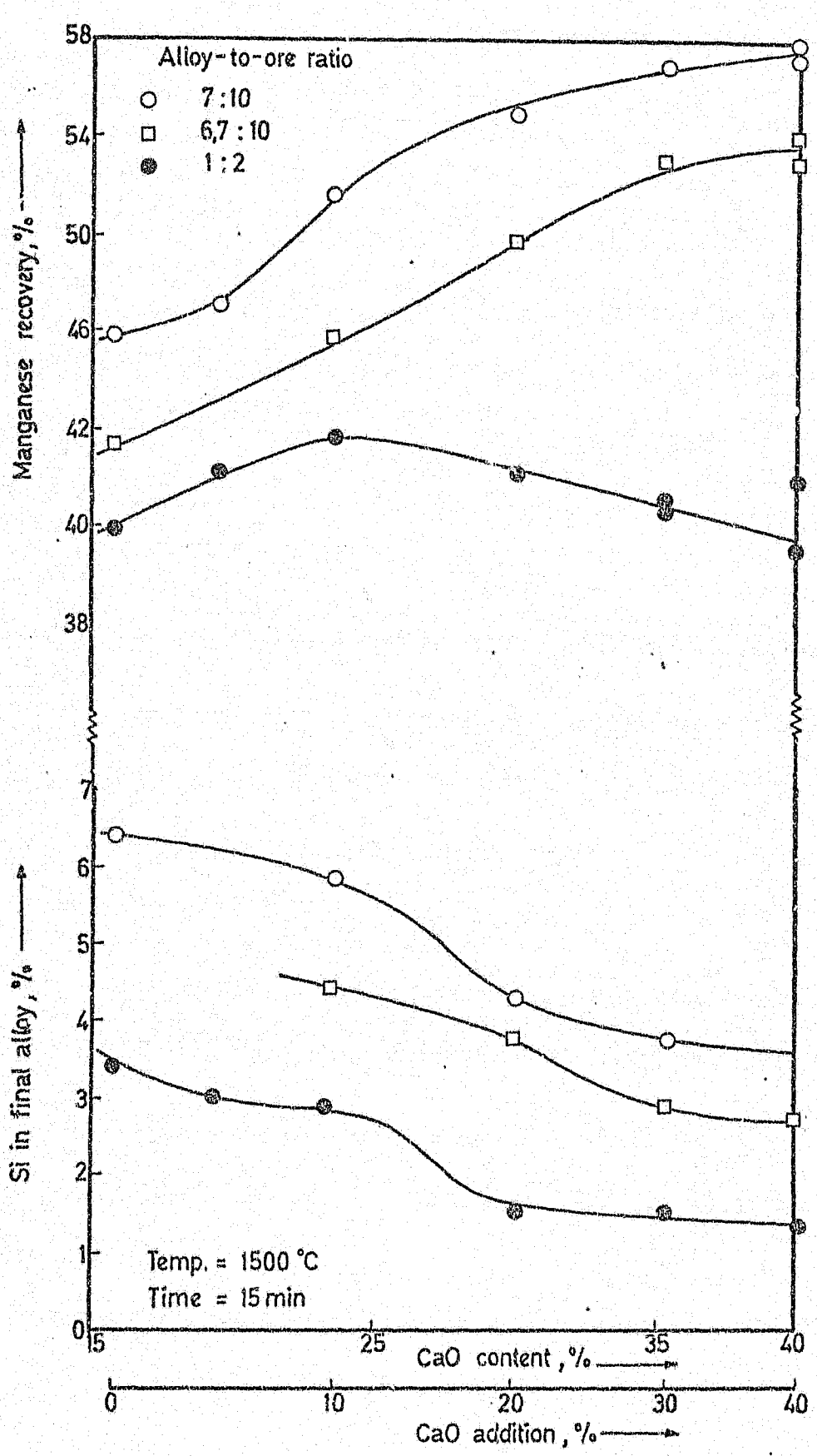


Figure 39. Effect of CaO on manganese recovery and the silicon content of the final alloy.

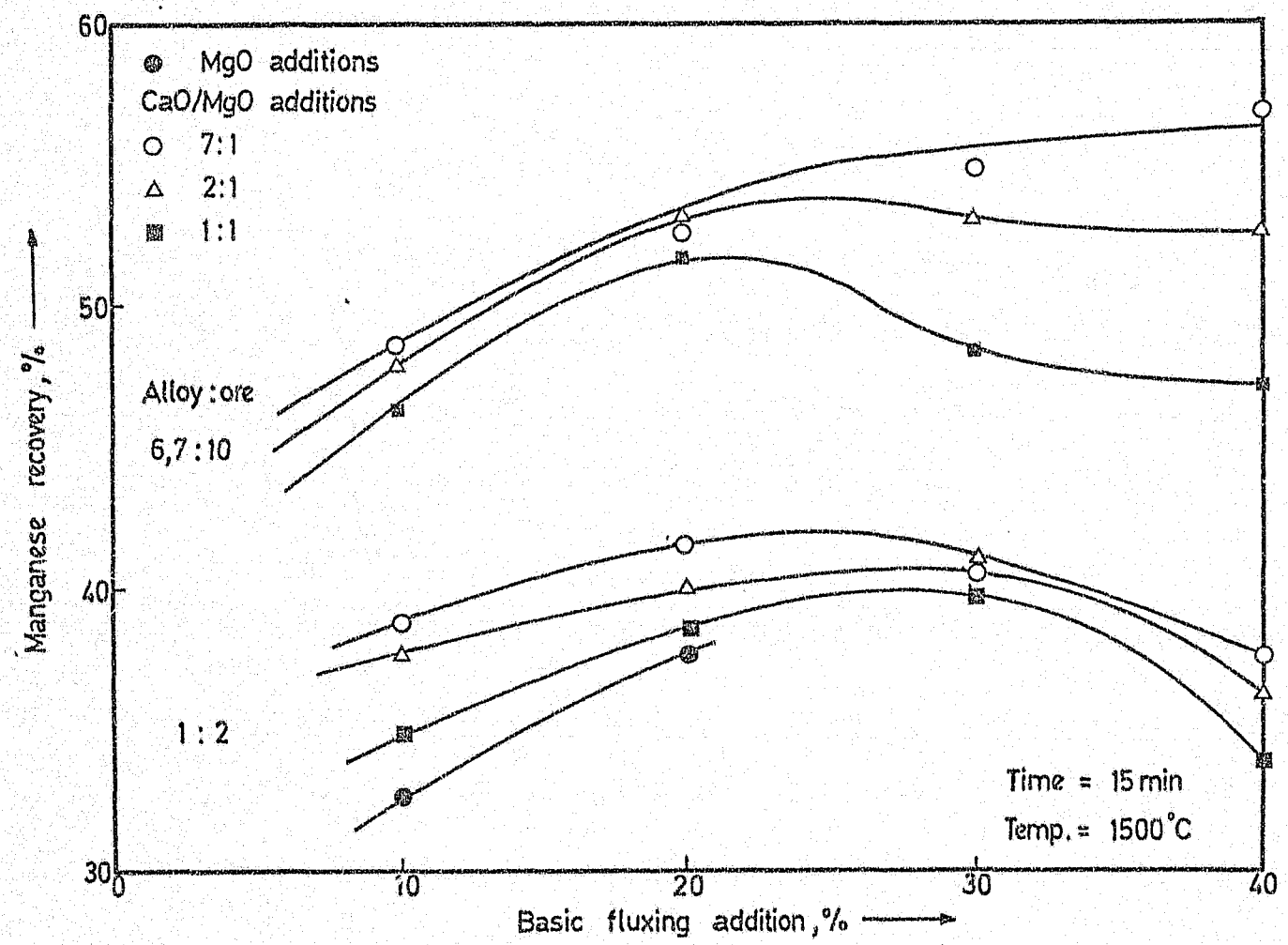


Figure 40. Effect of CaO-to-MgO ratio on manganese recovery.

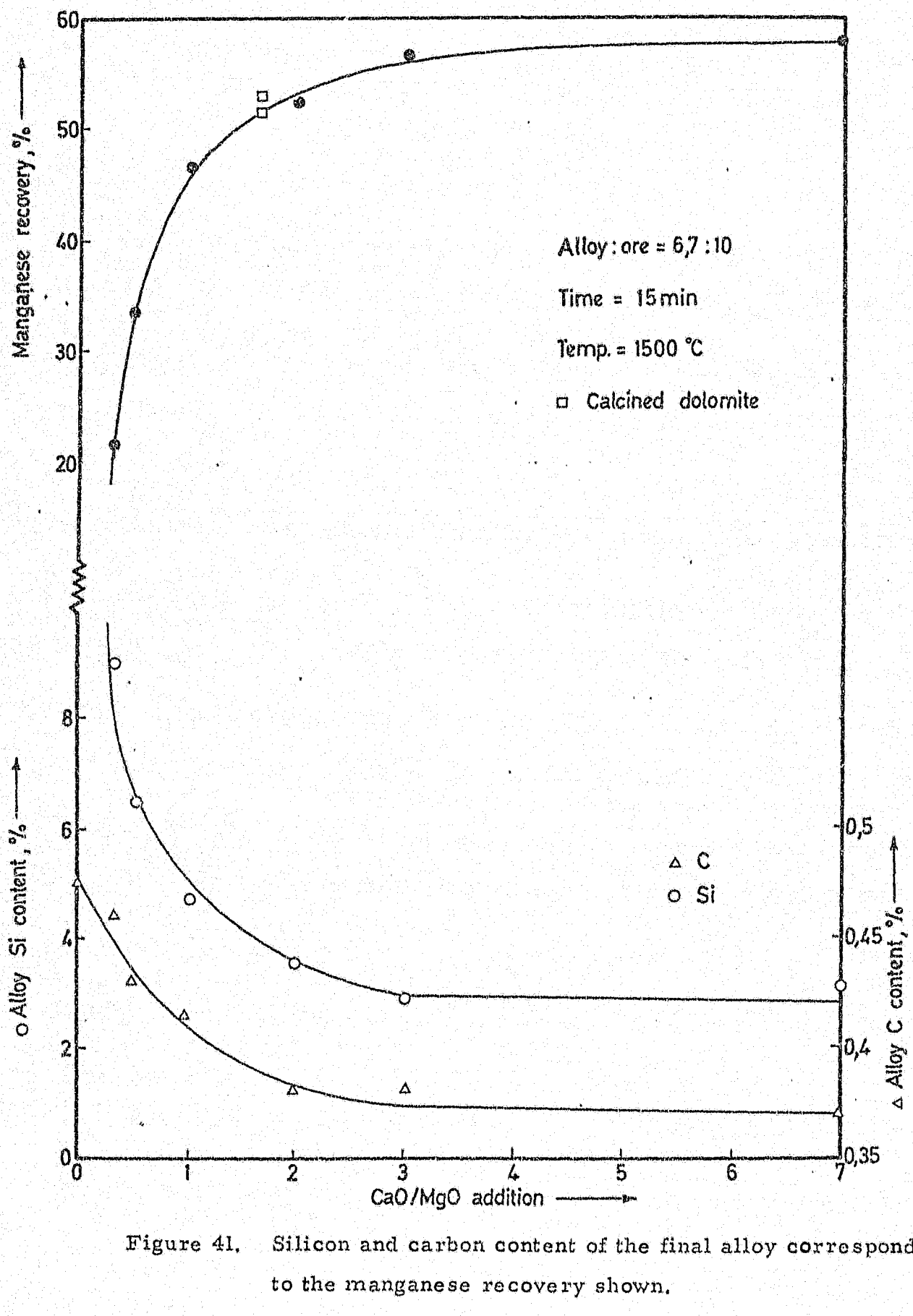


Figure 41. Silicon and carbon content of the final alloy corresponding to the manganese recovery shown.

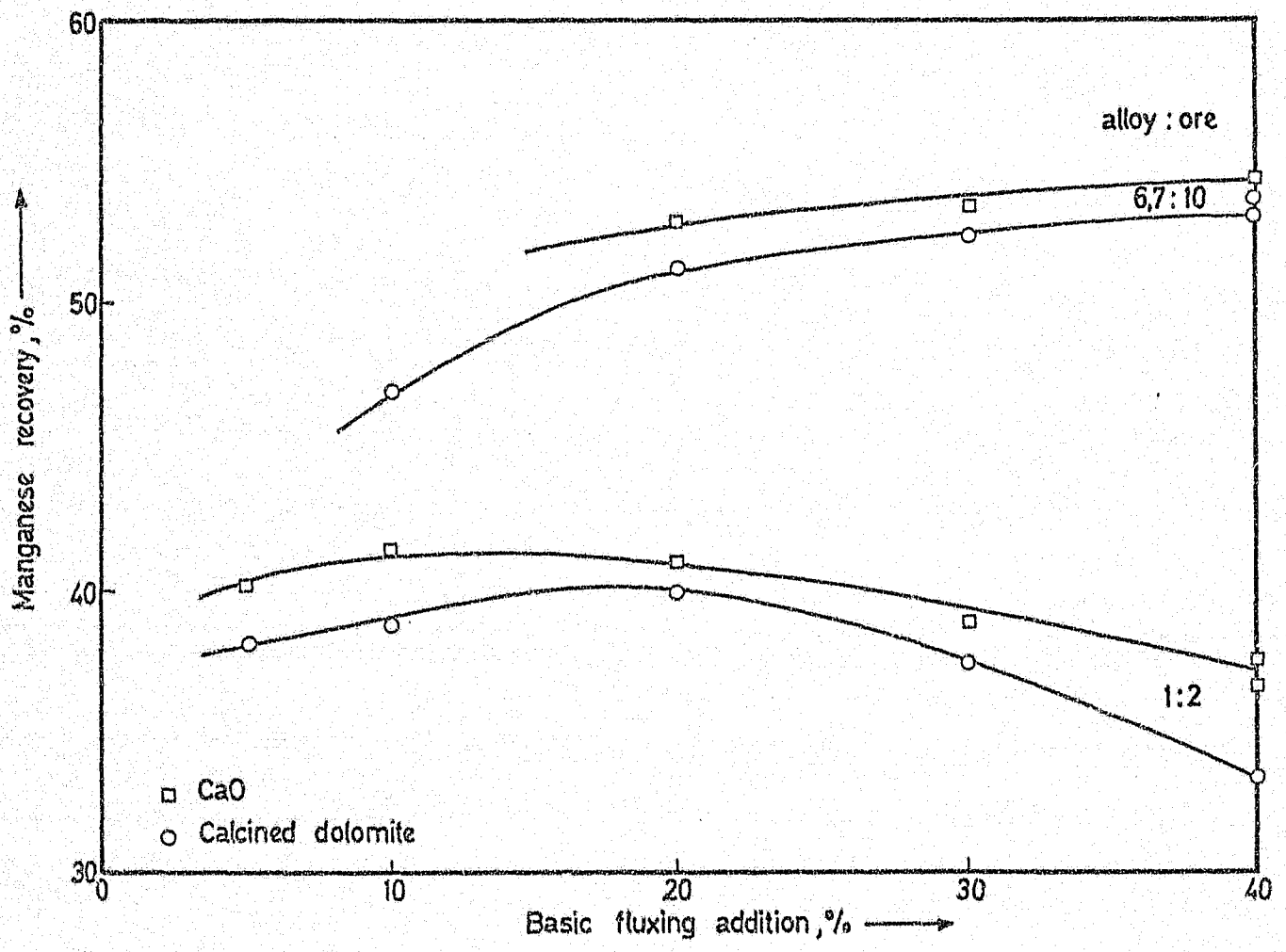


Figure 42. Comparisons of manganese recoveries when lime and calcined dolomite are used as fluxes.

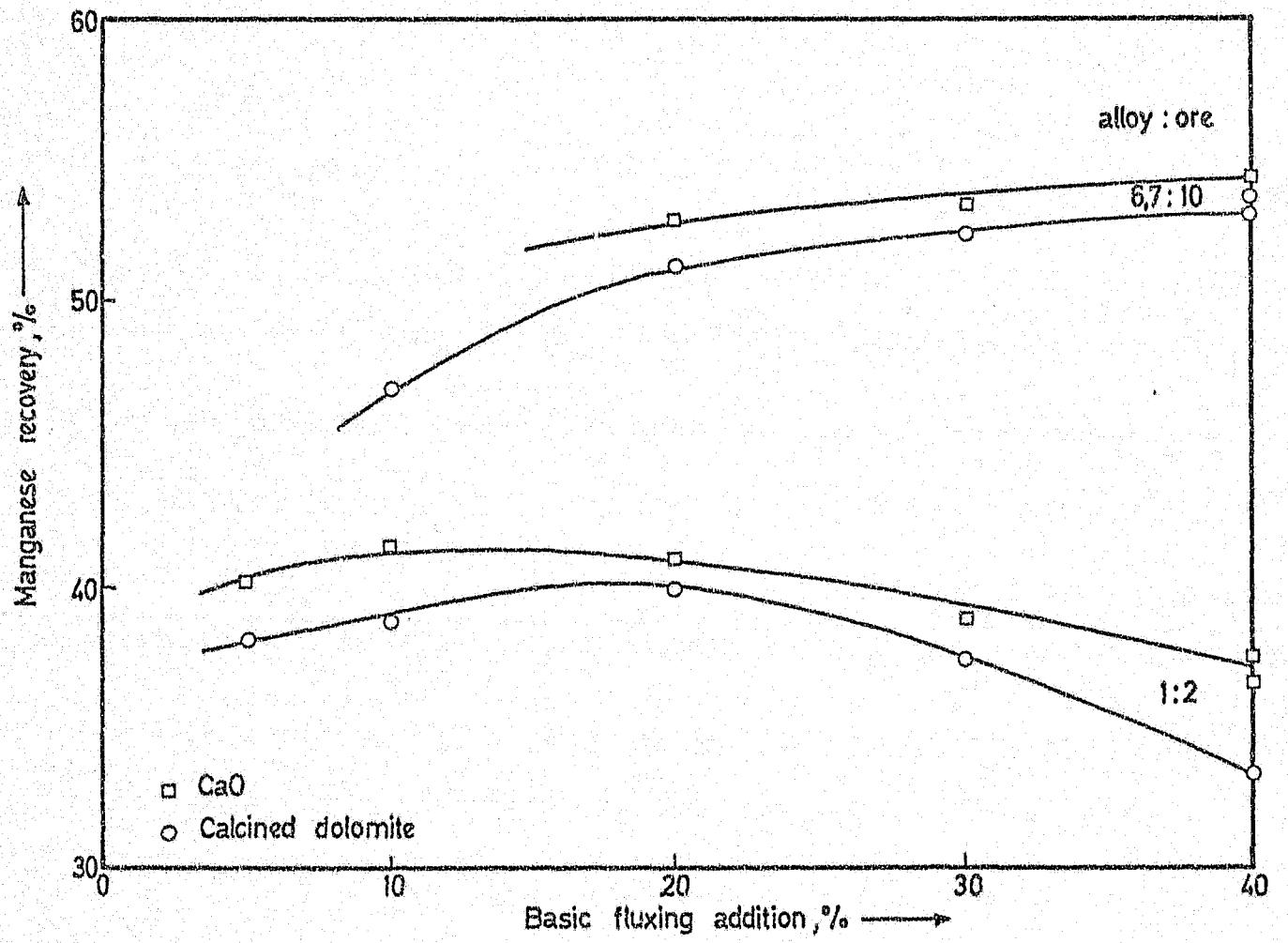


Figure 42. Comparisons of manganese recoveries when lime and calcined dolomite are used as fluxes.

MgO additions is to increase the manganese recovery, although it can be observed in Figure 40 that at any level of flux addition, as MgO replaces CaO there is a decrease in the manganese recovery.

Figure 41 shows manganese recovery as a function of the CaO - to - MgO ratio at a constant flux addition of 40 mass per cent. There is a decline in manganese recovery when the CaO - to - MgO ratio falls below 3.

The final fluxing addition was a calcined dolomite of the Transvaal Dolomite Series. The analysis of this calcine is given in Table 3. Figure 42 compares manganese recoveries when both lime and calcined dolomite are used as fluxes at two different alloy - to - ore ratios. For any particular alloy - to - ore ratio, calcined dolomite gives a slight loss in manganese recovery compared to the corresponding amount of CaO. If an alloy - to - ore ratio of 1 to 2 is used as in industrial practice, the difference in recoveries is only about 2 mass per cent and so use of dolomite might well be economically feasible provided it results in a fluid slag and easy arc furnace operation.

5.3 Reactions Involving Variations in the Mass and Composition of Reducing Alloy

Manganese recovery increased progressively as the mass of the industrial ferromanganese-silicide alloy was steadily increased as shown in Figure 43. Figure 44 shows the manganese recoveries and final alloy silicon levels obtained for variations in the silicon content of the alloy for an alloy - to - ore ratio of 1 to 2. The corresponding iron - to - manganese ratios for these synthetic alloys are shown in Table 5 and all experiments were conducted at 1500°C for 15 minutes.

Data for the silicothermic reduction of Mamatwan ore at increasing alloy - to - ore ratios are given in Figures 45 to 49. Figures 45 and 46 show the recoveries of manganese when various grades of ferromanganese silicide and ferrosilicon are used. In both cases maximum recovery is achieved for a 60 mass per cent

TABLE 5

SYNTHETIC FeMnSi REDUCING ALLOYS	
Silicon (%)	Fe-to-Mn ratio
5	0,118
10	0,125
15	0,134
20	0,143
30	0,167
40	0,200
50	0,250
65	0,400
80	1,000
90	0,000
100	0,000

silicon alloy. This substantial change in manganese recovery is even more marked when silicon metal is used as the reducing agent (Figure 49).

For small amounts of reducing agent, a steady increase in manganese recovery is obtained with increasing initial mass of silicon. In these cases, separation of the slag and alloy is very good and a very dense alloy is produced. For additions of more than 5, 5 grams of silicon, a decrease in manganese recovery is accompanied by poor separation of the slag and alloy and the alloy becomes more spherical. This phenomenon is illustrated in Figure 50. The large scatter in experimental results around this transition range suggests that manganese recoveries are very sensitive to small alterations in experimental conditions.

The use of aluminium as reducing agent together with silicon was investigated by reacting Fe-Mn-Si-Al alloys with a lime-ore melt containing a CaO addition of 20 mass per cent. The mass of silicon was kept constant and the aluminium content was varied. For a constant mass of silicon the ratio of manganese in the ore sample to silicon in the alloy is initially set at a value equivalent to that used industrially. From the variation of the aluminium content

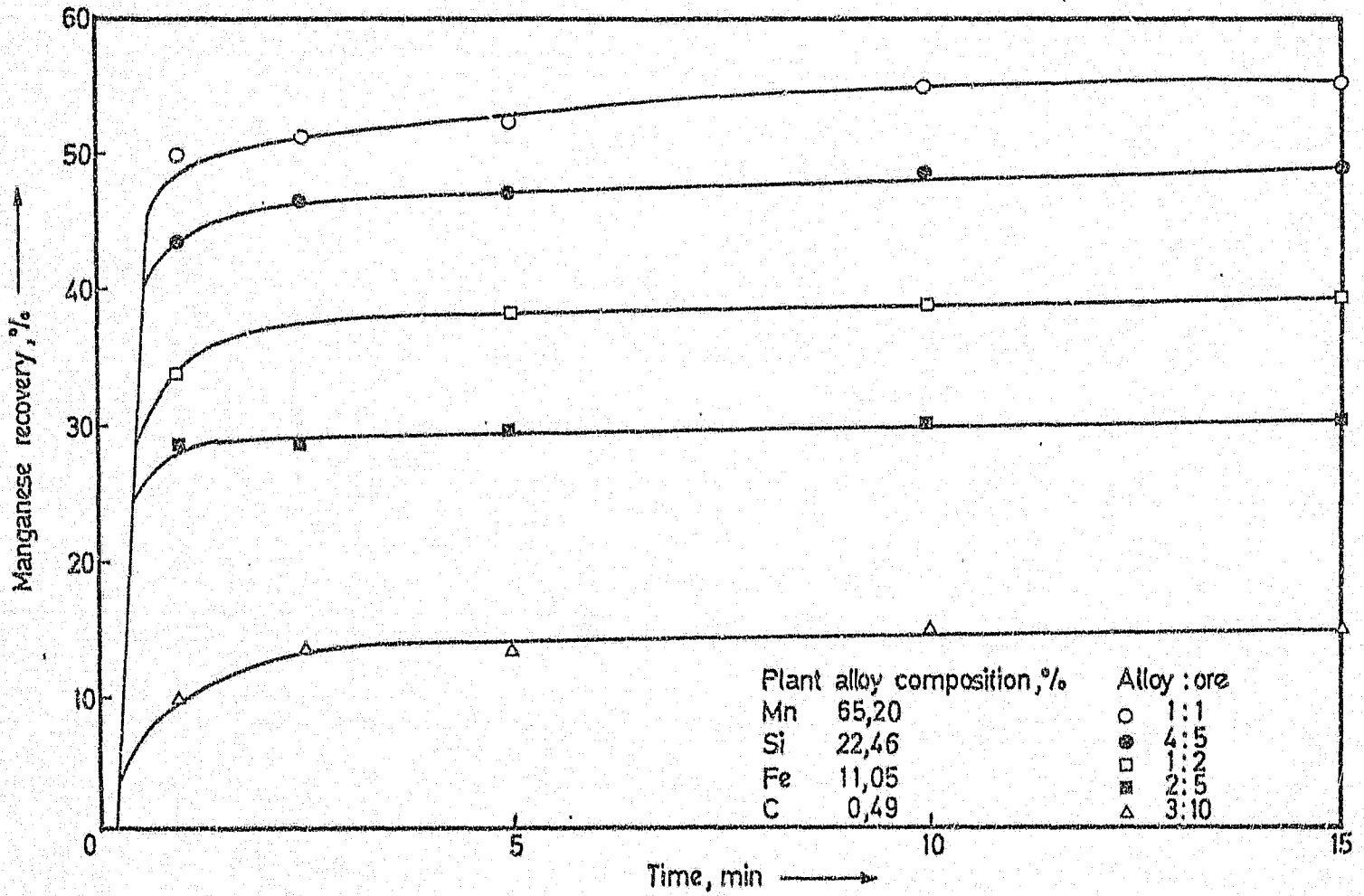


Figure 43. Increase in manganese recovery with time for increases in plant alloy-to-ore ratio without fluxing additions at 1500°C.

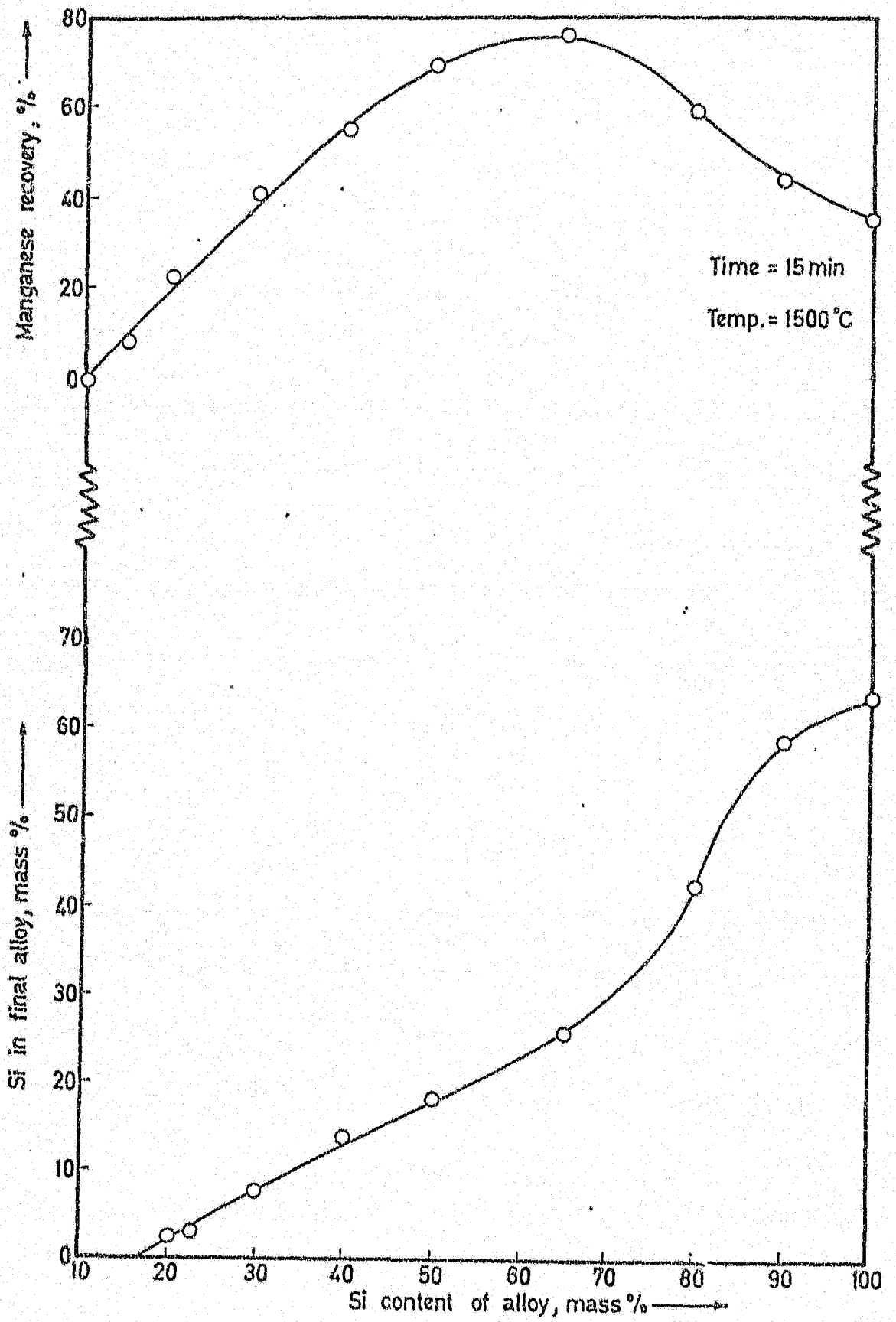


Figure 44 Manganese recovery and final alloy silicon content using a 1 to 2 alloy-to-ore ratio.

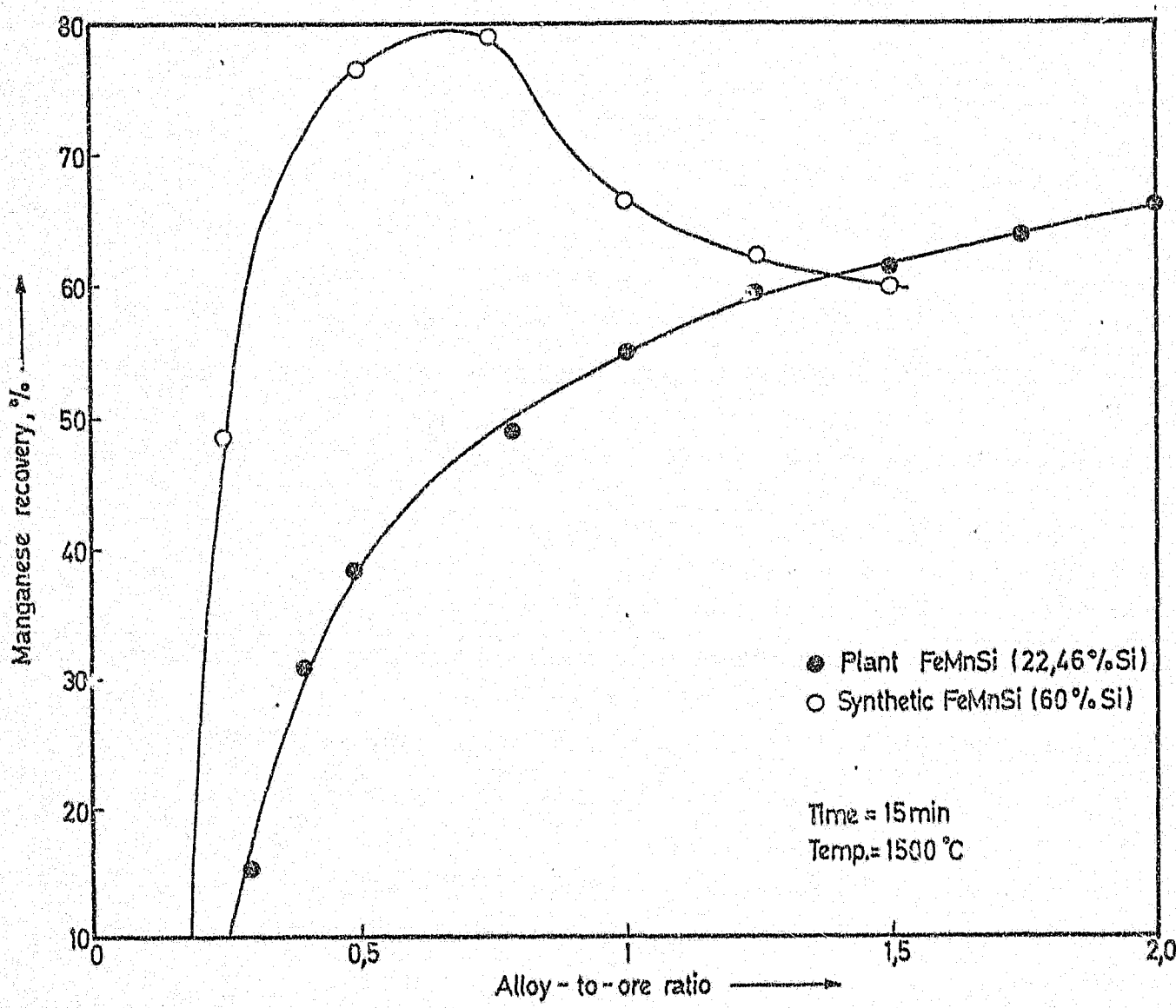


Figure 45. Comparison of manganese recovery using two ferromanganese-silicide reducing alloys.

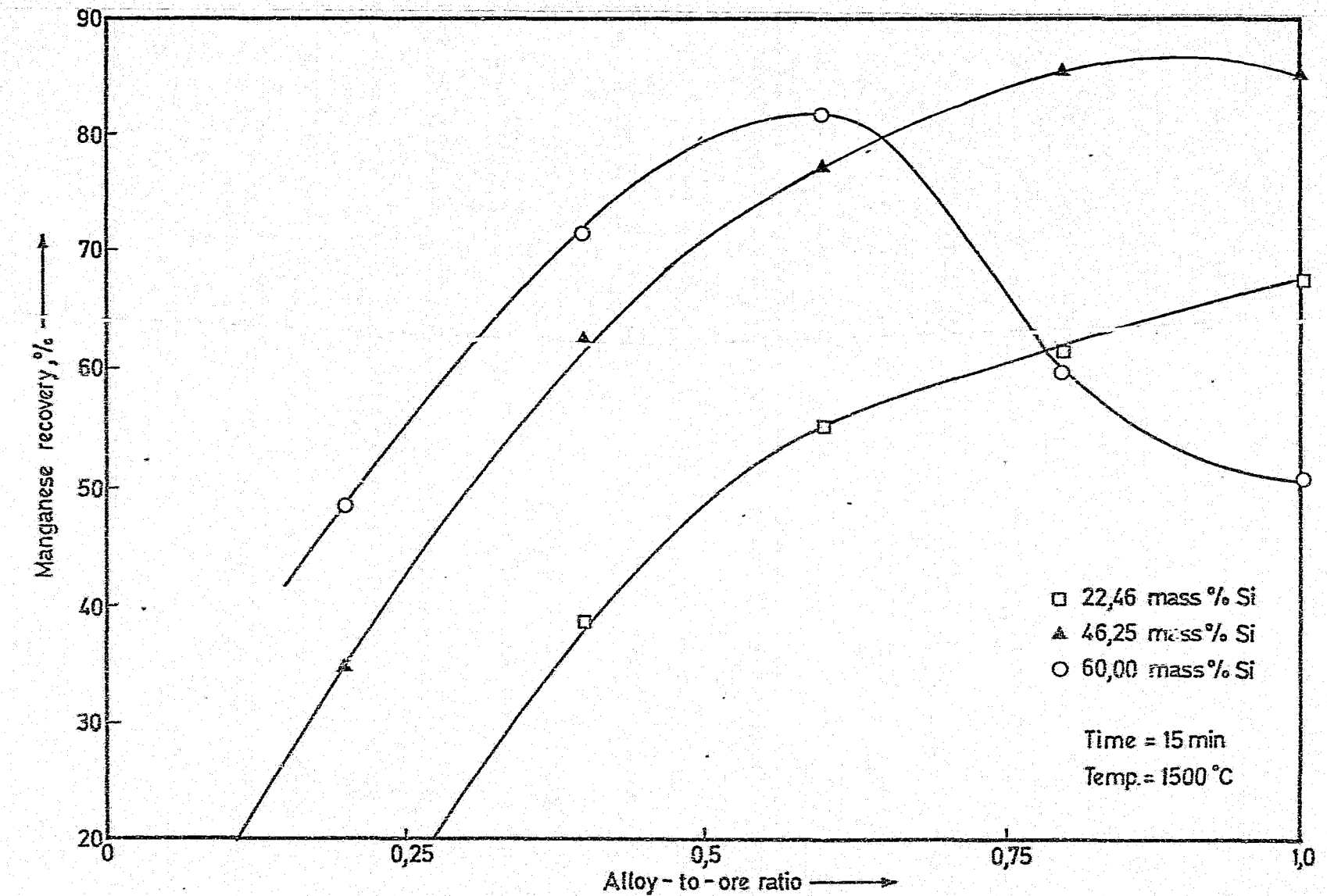


Figure 46. Comparison of manganese recovery for various grades of ferrosilicon.

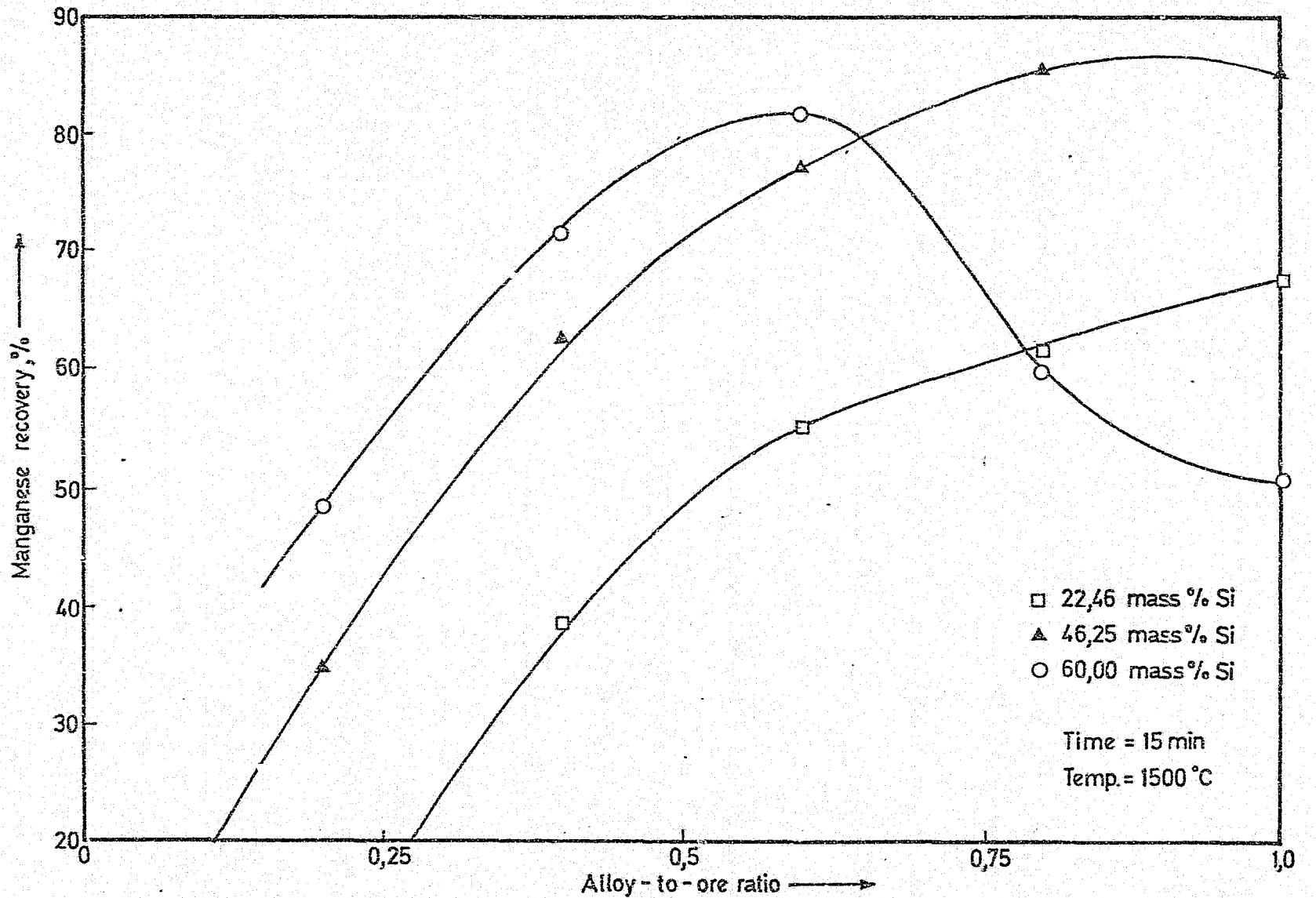


Figure 46. Comparison of manganese recovery for various grades of ferrosilicon.

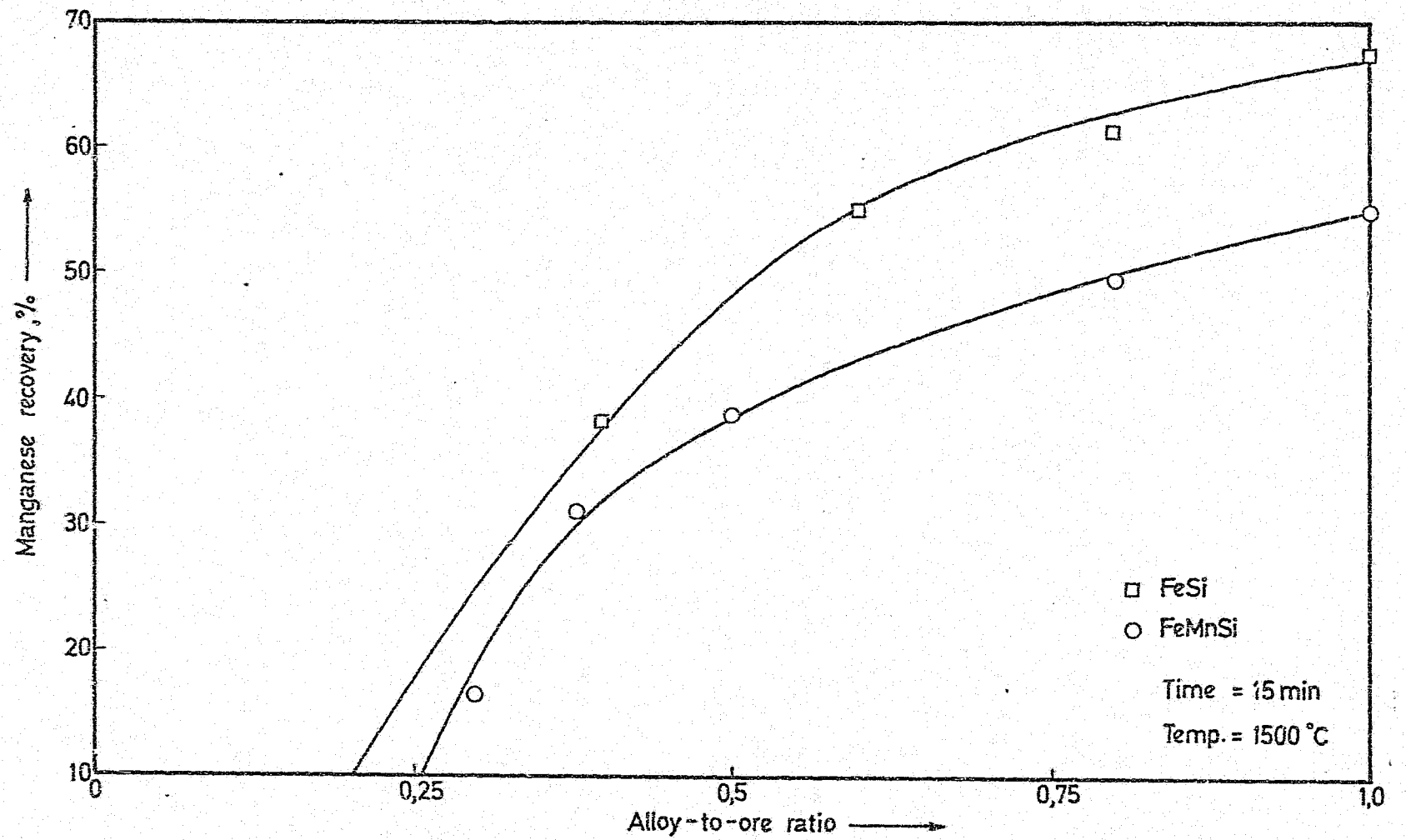


Figure 47. Comparison of manganese recovery using ferromanganese-silicide and ferrosilicon alloys each containing 22, 5 mass per cent silicon.

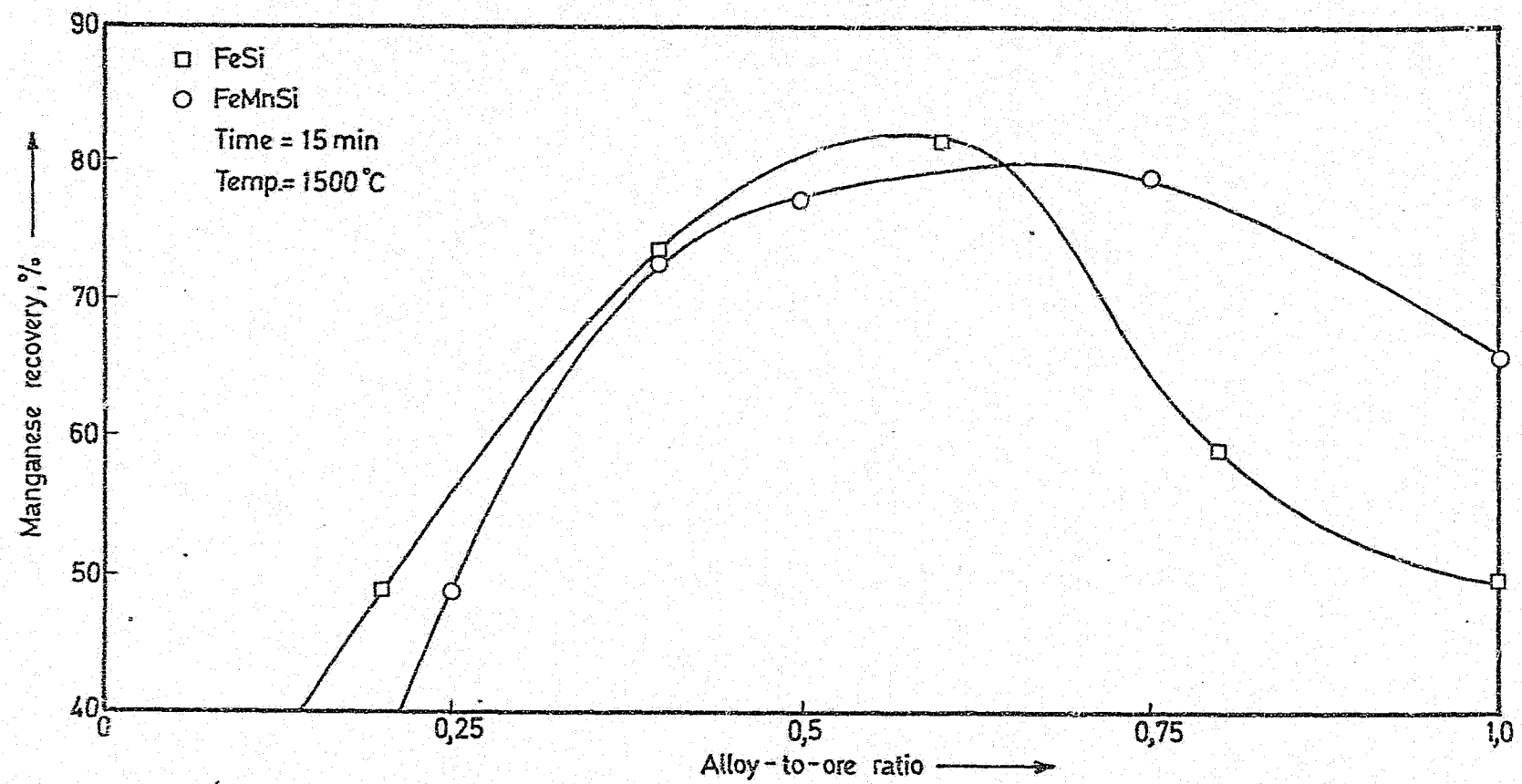


Figure 48. Comparison of manganese recovery using ferromanganese-silicide and ferrosilicon alloys containing 60 mass per cent silicon.

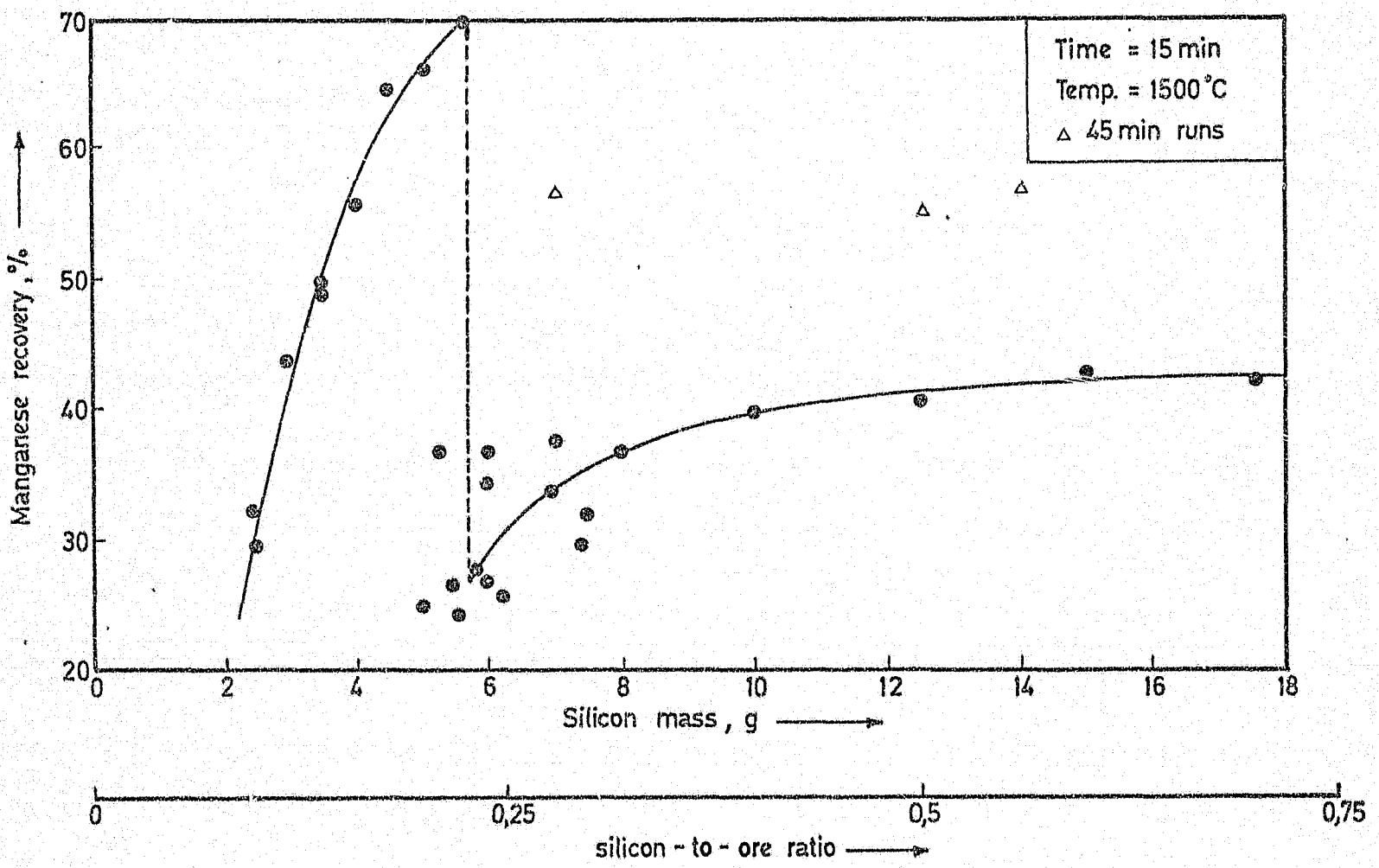


Figure 49. The variation of manganese recovery when silicon is used as reducing agent.



Figure 50. Final slag-alloy configuration when silicon is used as the reducing agent at
a) low silicon-to-ore ratios
b) high silicon-to ore ratios.

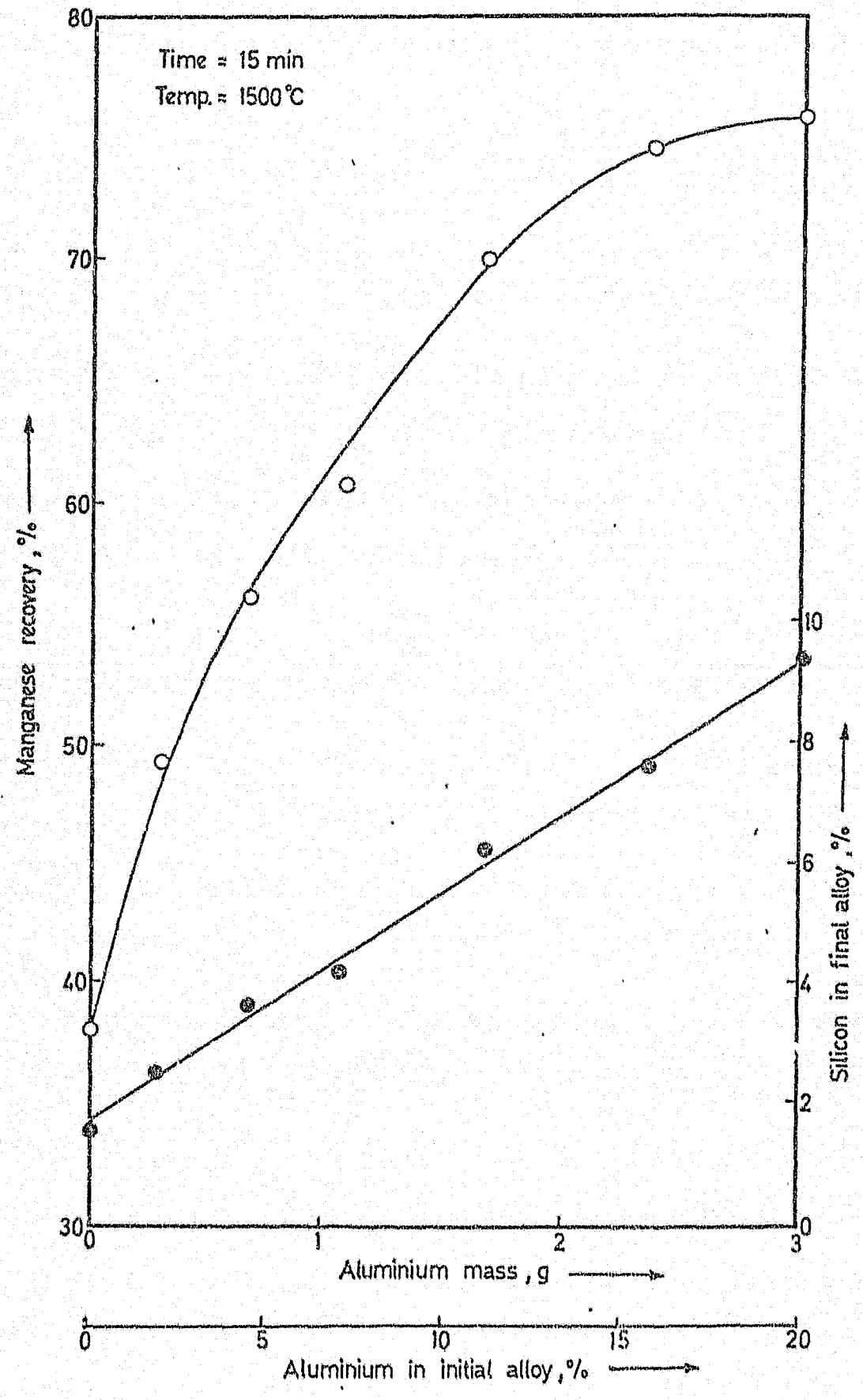


Figure 51. Manganese recovery related to aluminium addition. Samples contained the mass of silicon as used in the experiments with a 1 to 2 alloy-to-ore ratio where a plant alloy was utilized (22, 46% Si) .

of the reducing alloy it is possible to determine the improved recoveries. Figure 51 shows the manganese recoveries and the residual silicon levels in the final alloys. Final alloy aluminium contents were not plotted as the maximum value was only O, 3 mass per cent.

5.4 Stirring of the Reacting Melt

Stirring of the manganese - bearing slag has been conducted for an unfluxed reaction using a plant ferromanganese silicide alloy. Figure 52 shows that there is a decrease in manganese recovery with increased times of stirring. Stirring also decreased manganese recoveries at specific alloy silicon contents. There was no sign of physical entrapment of alloy particles in the final slag and the reductions in manganese recoveries by stirring cannot be explained on this basis.

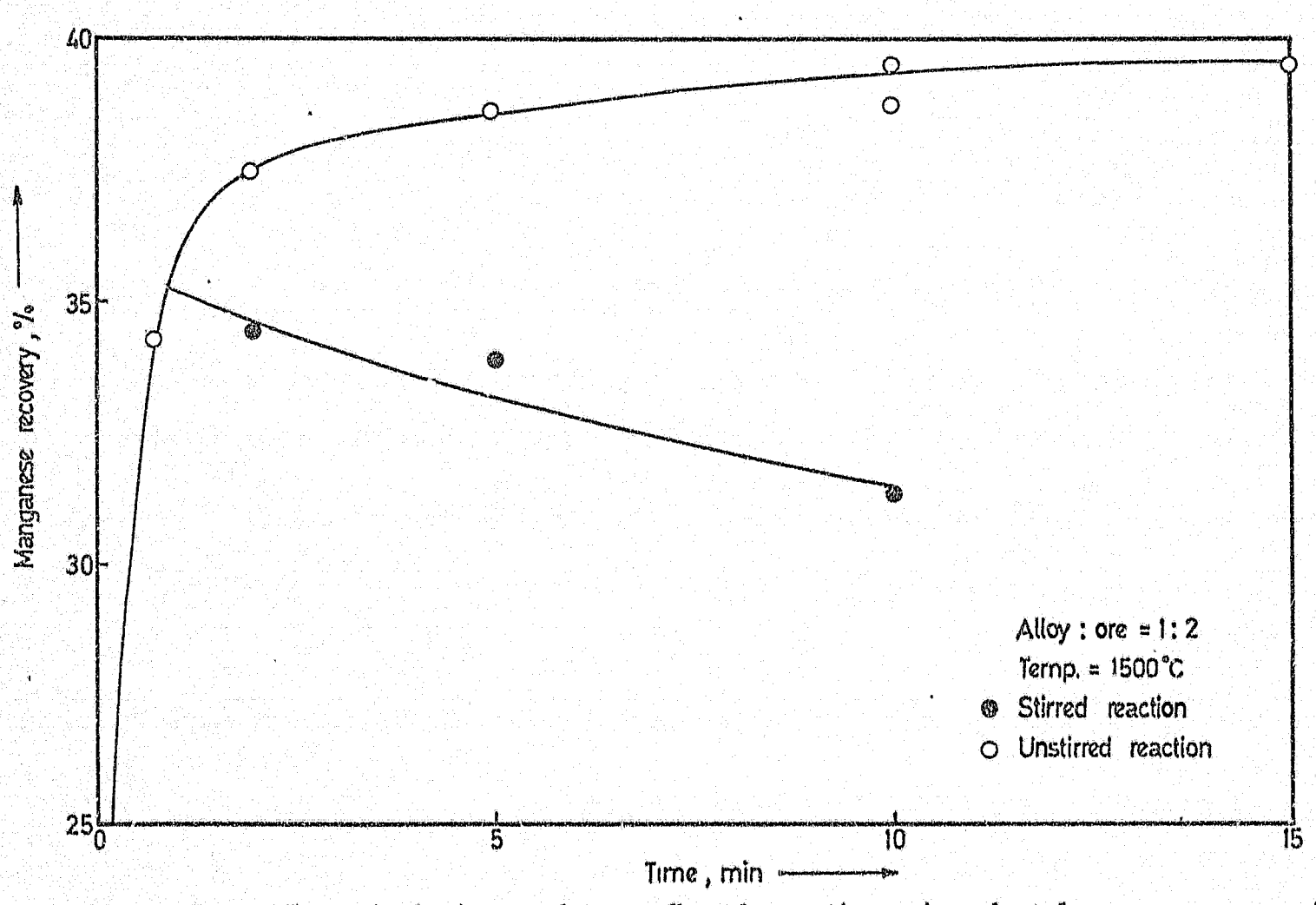


Figure 52. Effect of stirring on the non-fluxed reaction using plant ferromanganese-silicide.

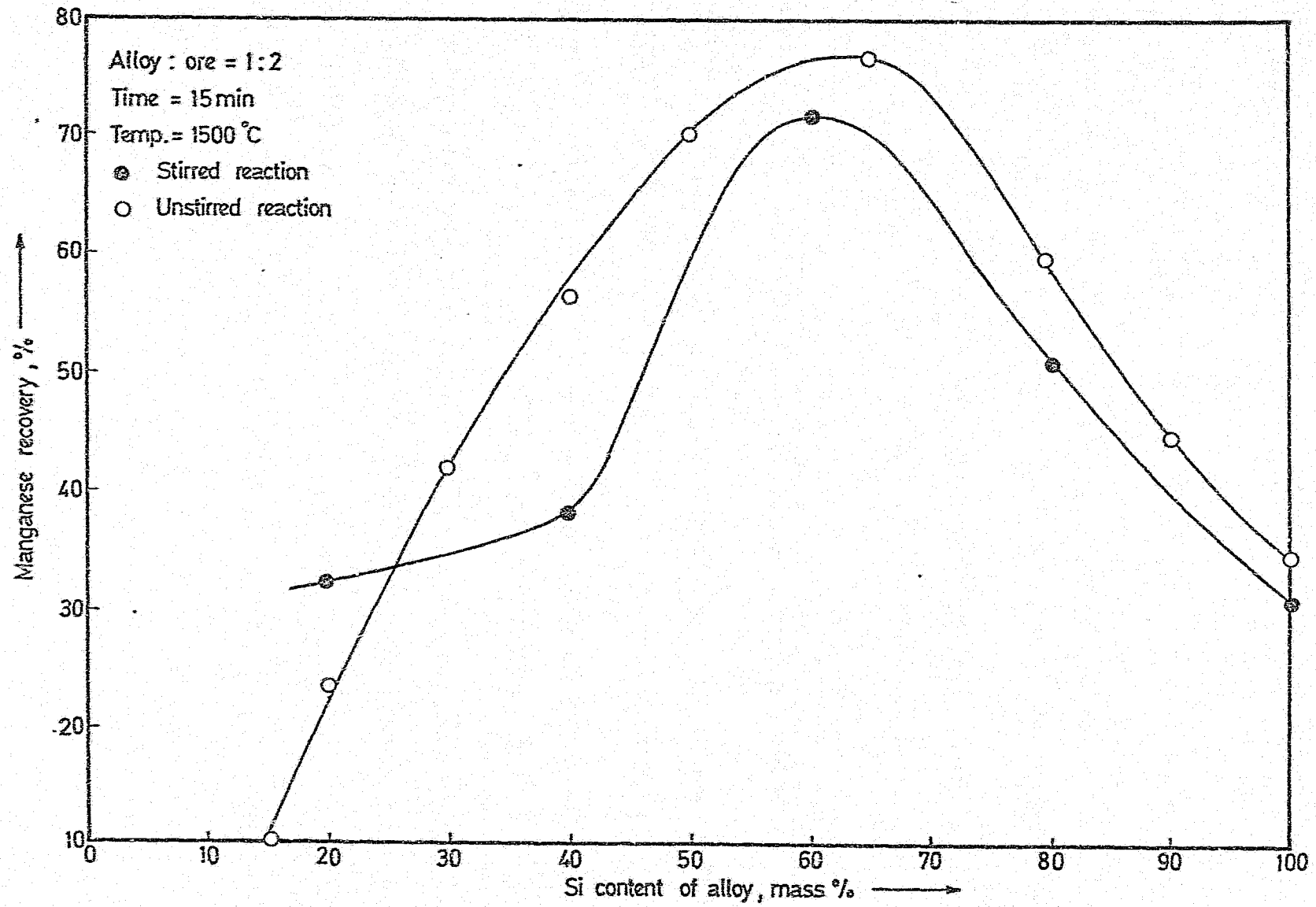


Figure 53. Effect of stirring on the non-fluxed reaction using synthetic ferromanganese-silicide.

6 DISCUSSION

6.1 Variables Affecting the Distribution of Manganese and Silicon between the Slag and the Alloy.

The many variables in the production of medium- and low - carbon ferromanganese should be optimized to ensure that Mamatwan manganese ore is used efficiently. To carry out this optimization, it is necessary to study slag - metal reactions for the production of medium - and low - carbon ferromanganese. The present investigation was aimed at understanding industrial practice and the experiments were designed to investigate important aspects of plant practice as much as was possible in small-scale experiments in the laboratory. It was anticipated that the data obtained could then be compared and related both to industrial practice and to more theoretical aspects of this slag - metal reaction.

The slag - metal reaction involved a violent silicothermic reduction reaction which caused a rapid and uncontrollable increase in the temperature of the reacting melt. This rapid temperature increase and violent reaction caused melt agitation which increased the rate of manganese transfer from the slag to the metal. However as it was impossible to maintain the melt temperature constant, no attempt was made to carry out a kinetic analysis of the rate of manganese and silicon transfer between the two phases.

6.1.1 Temperature

Considerable temperature variations were noted during the silicothermic reduction as shown in Figure 34. These temperature variations must accelerate the rate of manganese transfer between the slag and the alloy and the reaction reaches an apparent equilibrium within approximately two minutes from its commencement. Figure 35 shows that manganese recoveries from the slag differ only marginally when the initial temperature of reaction is varied from 1450

to 1600°C.

Daines and Pehlke[74] found that the rate of reduction of MnO from basic slags by silicon dissolved in liquid iron for silicon contents of up to approximately 4 mass per cent was controlled by diffusion of manganese in the iron phase and that temperature had little effect on the reduction rate. However, the tendency of increased temperature to favour increased manganese recovery in the metal may have been masked by evaporation in Daines and Pehlke's experiments. The influence of evaporation was reported by Filer and Darken[82] who studied the equilibrium between blast-furnace metal and slag. These workers found that at temperatures from 1500° to 1600°C, manganese concentrations in the metal phase increased considerably and then started to decrease whilst the MnO content of the slag continually decreased. and Darken explained this observation by manganese evaporation from the metallic phase with very little loss of aluminium or iron even at 1600°C.

At 1600°C the vapour pressure of pure Mn (p^{o}_{Mn}) is approximately O, O25 atm.[65] and if, the Fe-Mn-Si system is considered to be ideal then for a Fe - Mn-Si alloy containing 65 mass per cent manganese (X_{Mn} = O, 53) the vapour pressure above this alloy is given by the formula:

$$p_{Mn}(X_{Mn} = O, 53) = a_{Mn}(X_{Mn} = O, 53) \times p^{o}_{Mn}(X_{Mn} = 1) \qquad 6\ 1$$

Thus the vapour pressure established by the manganese above the alloy is O, O13 atm. (9, 88 mm Hg). at 1600°C. This vapour pressure is very much greater than the vapour pressures of silicon or iron above this alloy and thus selective vaporization of manganese may have occurred. The manganese mole fraction in blast-furnace metal is very much less than that in the Fe-Mn-Si alloy and this effect should be even greater than in the work of Filer and Darken[82].

For reaction times of 60 minutes at various reaction temperatures, manganese recovery declines to approximately 35 per cent This slight decrease in recovery can possibly be partially explained by

manganese evaporation losses which are very difficult to determine in this two-phase system during reaction.

The observed decrease in manganese recovery over extended time periods may also have occurred because of the achievement of an apparent equilibrium for a higher temperature than the nominal furnace temperature. The silicothermic reduction reaction generates considerable heat within the reacting melt and the resulting increase in melt temperature means that the manganese recovery is at least partially dependent on the melt temperature. As the melt temperature gradually decreases, the apparent equilibrium shifts to that for the lower temperatures giving a lower manganese recovery. This type of behaviour has also been reported by Filer and Darken[82].

No obvious increase in manganese recovery to the metal phase occurred during the fixed reaction time of 15 minutes for an increase in temperature from 1450 to 1600°C and therefore, as previously stated, 1500°C was selected as the furnace temperature for all the subsequent experiments.

6.1.2 Slag Basicity

The reaction for the recovery of manganese from a MnO rich slag is

$$2(MnO) + [Si] = (SiO_2) + 2[Mn] \quad \ldots\ldots\ldots \quad 6.2$$

It is not possible to predict the equilibrium distribution of manganese and silicon between the slag and the alloy because of the lack of fundamental data on the activities of components in both the slag and the alloy phases.

Before the study of Warren et al[7] no information had been published on the activity of MnO in the five - component system $CaO-MgO-MnO-Al_2O_3-SiO_2$. However the quaternary system $CaO-MnO-Al_2O_3-SiO_2$ had been studied by Turkdogan[72] and Mehta et al[40] who determined MnO activities at 1500°C and 1650°C respectively. The work of Warren et al gave values for the activity of MnO for MnO concentrations up to 20 mass per cent in the

$CaO-MgO-MnO-Al_2O_3-SiO_2$ system.

To determine the activity of MnO in slags used in the production of medium - and low - carbon ferromanganese, higher concentrations of MnO must be considered and at present activity data is not available at these higher concentrations. In addition data on the activities of components in the Fe-Mn-Si and Fe-Mn-Si-C systems have not been published.

To overcome the problems caused by this lack of fundamental data, an apparent equilibrium constant K'_{Mn-Si} has been defined[83] from equation 6.2as

$$K'_{Mn-Si} = \frac{(MnO)\sqrt{[Si]}}{[Mn]} \qquad \ldots\ldots\ldots\ldots \quad 6.3$$

where concentrations are given in mass fractions.

The apparent equilibrium constant depends mainly on the manganese distribution ratio which is close to its equilibrium value in practice, whilst the silicon distribution is far removed from equilibrium[27].

Schenck et al[68, 69] used this apparent equilibrium constant to study the distribution of manganese between Mn-Si-Fe alloys and MnO containing slags over the temperature range 1450 to 1550°C. As the conditions in the slag-metal study of Schenck et al correspond closely to those in the present investigation, apparent equilibrium constants can be compared. Schenck et al[68, 69] found that pseudo-equilibrium conditions were set up rapidly between the MnO in the slag and the manganese in the metal phase and at a temperature of 1500°C K'_{Mn-Si} varied from $8,7 \times 10^{-2}$ to $4,2 \times 10^{-2}$ as the slag basicity ratio increased from 0,6 to 1,6. Slag basicity ratio was defined as $(CaO + MgO)/SiO_2$ where all values of the concentrations of slag components are expressed in mass per cent.

Detailed summaries of the silicothermic reduction reaction for the present investigation are shown in Tables 6 to 9 for considerable variations in the amounts and types of fluxing additions and in the silicon contents of the Tables 6 to 8 show values of K'_{Mn-Si} for this

TABLE 6

DISTRIBUTION OF MANGANESE AND SILICON BETWEEN THE ALLOY AND THE SLAG FOR THE LIME FLUXED REACTION WITH PLANT FeMnSi AS REDUCING AGENT

Alloy-to-ore ratio	CaO addition (%)	Final compositions: Alloy (mass fraction) Mn	Alloy Si	Slag (mass fraction) MnO	Slag SiO_2	Slag CaO	Slag MgO	Distribution ratios $\frac{(MnO)}{Mn}$	Distribution ratios $\frac{(SiO_2)}{Si}$	Basicity ratio $\frac{CaO + MgO}{SiO_2}$	Apparent equilibrium constant $K=\frac{[Mn]^2(SiO_2)}{(MnO)^2[Si]}$	Apparent equilibrium constant $K_1'=\frac{(MnO)\sqrt{[Si]}}{[Mn]}$
1:2	0	0,790	0,030	0,373	0,300	0,168	0,034	0,46	8,56	0,67	40,7	0,086
	10	0,798	0,028	0,314	0,272	0,245	0,031	0,39	9,81	1,01	62,5	0,066
	20	0,811	0,019	0,281	0,242	0,324	0,028	0,35	13,00	1,45	134,3	0,042
	30	0,817	0,015	0,263	0,218	0,385	0,025	0,32	14,50	1,88	140,5	0,039
	40	0,827	0,013	0,245	0,198	0,432	0,023	0,30	15,10	2,30	173,6	0,034
6,7:10	0	0,780	0,054	0,360	0,303	0,154	0,034	0,46	5,61	0,62	26,3	0,110
	10	0,795	0,045	0,300	0,282	0,252	0,031	0,38	6,27	1,00	44,5	0,081
	20	0,801	0,037	0,253	0,266	0,333	0,028	0,32	7,19	1,36	71,2	0,061
	30	0,814	0,028	0,218	0,248	0,369	0,025	0,27	8,86	1,70	123,3	0,045
	40	0,819	0,026	0,196	0,229	0,448	0,023	0,24	8,80	2,06	153,0	0,039
7:10	0	0,789	0,065	0,334	0,321	0,158	0,035	0,42	2,43	0,60	27,5	0,107
	10	0,799	0,059	0,269	0,304	0,258	0,032	0,34	5,15	0,95	46,2	0,083
	20	0,814	0,043	0,228	0,283	0,337	0,029	0,28	7,84	1,29	75,0	0,058
	30	0,819	0,038	0,198	0,261	0,401	0,026	0,24	6,87	1,64	117,5	0,047
	40	0,821	0,036	0,177	0,241	0,454	0,024	0,22	6,70	1,98	147,7	0,042

TABLE 6

DISTRIBUTION OF MANGANESE AND SILICON BETWEEN THE ALLOY AND THE SLAG FOR THE LIME FLUXED REACTION WITH PLANT FeMnSi AS REDUCING AGENT

Alloy-to-ore ratio	CaO addition (%)	Final compositions: Alloy (mass fraction) Mn	Alloy Si	Slag (mass fraction) MnO	Slag SiO_2	Slag CaO	Slag MgO	Distribution ratios $\frac{(MnO)}{Mn}$	Distribution ratios $\frac{(SiO_2)}{Si}$	Basicity ratio $\frac{CaO + MgO}{SiO_2}$	Apparent equilibrium constant $K=\frac{[Mn]^2(SiO_2)}{(MnO)^2[Si]}$	Apparent equilibrium constant $K_1'=\frac{(MnO)\sqrt{[Si]}}{[Mn]}$
1:2	0	0,790	0,030	0,373	0,300	0,168	0,034	0,46	8,56	0,67	40,7	0,086
	10	0,798	0,028	0,314	0,272	0,245	0,031	0,39	9,81	1,01	62,5	0,066
	20	0,811	0,019	0,281	0,242	0,324	0,028	0,35	13,00	1,45	134,3	0,042
	30	0,817	0,015	0,263	0,218	0,385	0,025	0,32	14,50	1,88	140,5	0,039
	40	0,827	0,013	0,245	0,198	0,432	0,023	0,30	15,10	2,30	173,6	0,034
6,7:10	0	0,780	0,054	0,360	0,303	0,154	0,034	0,46	5,61	0,62	26,3	0,110
	10	0,795	0,045	0,300	0,282	0,252	0,031	0,38	6,27	1,00	44,5	0,081
	20	0,801	0,037	0,253	0,266	0,333	0,028	0,32	7,19	1,36	71,2	0,061
	30	0,814	0,028	0,218	0,248	0,369	0,025	0,27	8,86	1,70	123,3	0,045
	40	0,819	0,026	0,196	0,229	0,448	0,023	0,24	8,80	2,06	153,0	0,039
7:10	0	0,789	0,065	0,334	0,321	0,158	0,035	0,42	2,43	0,60	27,5	0,107
	10	0,799	0,059	0,269	0,304	0,258	0,032	0,34	5,15	0,95	46,2	0,083
	20	0,814	0,043	0,228	0,283	0,337	0,029	0,28	7,84	1,29	75,0	0,058
	30	0,819	0,038	0,198	0,261	0,401	0,026	0,24	6,87	1,64	117,5	0,047
	40	0,821	0,036	0,177	0,241	0,454	0,024	0,22	6,70	1,98	147,7	0,042

TABLE 7

DISTRIBUTION OF MANGANESE AND SILICON BETWEEN THE SLAG AND THE ALLOY FOR A PLANT ALLOY-TO-ORE RATIO OF 6,7 TO 10 WHEN MAGNESIA REPLACES LIME AS A FLUX

Flux addition		Final Compositions						Distribution ratios		Basicity ratio	Apparent equilibrium constant,	
		Alloy (mass fraction)		Slag (mass fraction)				$\frac{(MnO)}{Mn}$	$\frac{(SiO_2)}{Si}$	$\frac{CaO + MgO}{SiO_2}$	$K = \frac{[Mn]^2(SiO_2)}{(MnO)^2[Si]}$	$K_1 = \frac{(MnO)\sqrt{[Si]}}{[Mn]}$
$\frac{CaO}{MgO}$	Mass %	Mn	Si	MnO	SiO_2	CaO	MgO					
7:1	10	0,773	0,076	0,286	0,291	0,234	0,045	0,370	3,83	0,98	28,0	0,102
	20	0,780	0,071	0,241	0,274	0,308	0,054	0,309	3,86	1,32	40,7	0,082
	30	0,786	0,067	0,206	0,265	0,364	0,061	0,262	3,96	1,60	58,5	0,068
	40	0,789	0,064	0,181	0,239	0,410	0,067	0,229	3,73	2,00	70,8	0,058
2:1	10	0,770	0,078	0,288	0,291	0,241	0,045	0,374	3,73	0,98	26,5	0,104
	20	0,780	0,071	0,237	0,263	0,308	0,084	0,304	3,71	1,30	42,3	0,081
	30	0,780	0,071	0,215	0,252	0,361	0,120	0,276	3,55	1,67	46,5	0,073
	40	0,780	0,071	0,200	0,227	0,405	0,136	0,256	3,20	2,07	49,3	0,068
1:1	10	0,769	0,079	0,296	0,286	0,238	0,085	0,372	3,62	0,99	24,5	0,104
	20	0,780	0,071	0,241	0,274	0,308	0,124	0,351	3,36	1,32	40,7	0,097
	30	0,773	0,076	0,235	0,239	0,356	0,160	0,309	3,14	1,74	34,0	0,085
	40	0,773	0,076	0,214	0,218	0,401	0,195	0,282	2,87	2,14	37,2	0,078

TABLE 8

DISTRIBUTION OF MANGANESE AND SILICON BETWEEN THE SLAG AND THE ALLOY FOR A PLANT ALLOY-TO-ORE RATIO OF 1 TO 2 WHEN MAGNESIA REPLACES LIME AS A FLUX

Flux addition		Final compositions						Distribution ratios		Basicity ratio	Apparent equilibrium constant	
		Alloy (mass fraction)		Slag (mass fraction)							$K=\frac{[Mn]^2(SiO_2)}{(MnO)^2[Si]}$	$K_1=\frac{(MnO)\sqrt{[Si]}}{[Mn]}$
$\frac{CaO}{MgO}$	Mass %	Mn	Si	MnO	SiO_2	CaO	MgO	$\frac{(MnO)}{Mn}$	$\frac{(SiO_2)}{Si}$	$\frac{CaO+MgO}{SiO_2}$		
7:1	10	0,790	0,044	0,327	0,264	0,233	0,044	0,41	6,00	1,05	35,9	0,086
	20	0,798	0,039	0,283	0,246	0,300	0,052	0,36	6,30	1,43	50,5	0,071
	30	0,789	0,047	0,266	0,214	0,352	0,059	0,34	5,55	1,92	40,4	0,073
	40	0,786	0,048	0,253	0,191	0,391	0,064	0,33	3,98	2,38	51,6	0,071
2:1	10	0,789	0,047	0,336	0,257	0,209	0,066	0,43	5,47	1,07	30,2	0,093
	20	0,795	0,043	0,291	0,240	0,256	0,093	0,39	5,58	1,46	70,2	0,077
	30	0,800	0,041	0,261	0,220	0,294	0,115	0,35	5,37	1,86	50,3	0,067
	40	0,786	0,048	0,256	0,193	0,321	0,131	0,33	4,02	2,34	38,4	0,072
1:1	10	0,780	0,052	0,345	0,251	0,190	0,083	0,44	4,83	1,09	54,5	0,100
	20	0,788	0,046	0,299	0,235	0,222	0,125	0,38	5,11	1,48	35,6	0,082
	30	0,795	0,043	0,265	0,219	0,248	0,160	0,36	5,37	1,86	46,1	0,074
	40	0,778	0,053	0,263	0,188	0.265	0,186	0,34	3,55	2,40	30,8	0,078
0	10	0,756	0,054	0,353	0,245	0,134	0,138	0,46	4,54	1,11	20,9	0,107
	20	0,788	0,046	0,299	0,235	0,123	0,255	0,38	5,10	1,48	35,6	0,081

investigation over a wider range of basicity ratios than that considered by Schenck[68, 69]. The tables also show a lowering in the apparent equilibrium constant with slag basicity increases where values are similar to the range reported by Schenck.

A summary of the effects of types and quantities of fluxing additions on the apparent equilibrium reaction may be obtained from Tables 6 to 8. As the amount of basic fluxing component and hence slag basicity is increased at any particular alloy-to-ore ratio there is a decrease in the value of the apparent equilibrium constant.

The manganese distribution ratio is defined as (MnO)/ [Mn] where (MnO) represents the MnO content of the final slag and [Mn] represents the manganese concentration of the final alloy and for the maximum recovery of manganese from a manganese ore this ratio should be as low as possible. Similarly, the silicon distribution ratio is defined as (SiO_2)/ [Si] where (SiO_2) represents the silica content of the final slag and [Si] the silicon concentration of the final alloy. In a refined ferromanganese, the alloy silicon concentration should be low giving a high value for the silicon distribution ratio.

To meet market specifications, industrial processes for the production of medium - and low-- carbon ferromanganese must produce an alloy with a silicon content of less than 1, 5 mass per cent and a manganese content of approximately 80 per cent. At the same time manganese must be extracted from the ore as efficiently as possible.

In practice, the silicon and manganese distribution ratios are such that these two conditions cannot be satisfied simultaneously. The ferromanganese producer normally decides to produce a highly refined alloy and to accept a higher loss of manganese to the slag. Hence, in industrial processes, it is more important to maintain high values of the silicon distribution ratio than to maintain low values of the manganese distribution ratio provided that the manganese content in the alloy is maintained at approximately 80 per cent.

Figures 54 to 56 from the data in Tables 6 to 8 respectively show

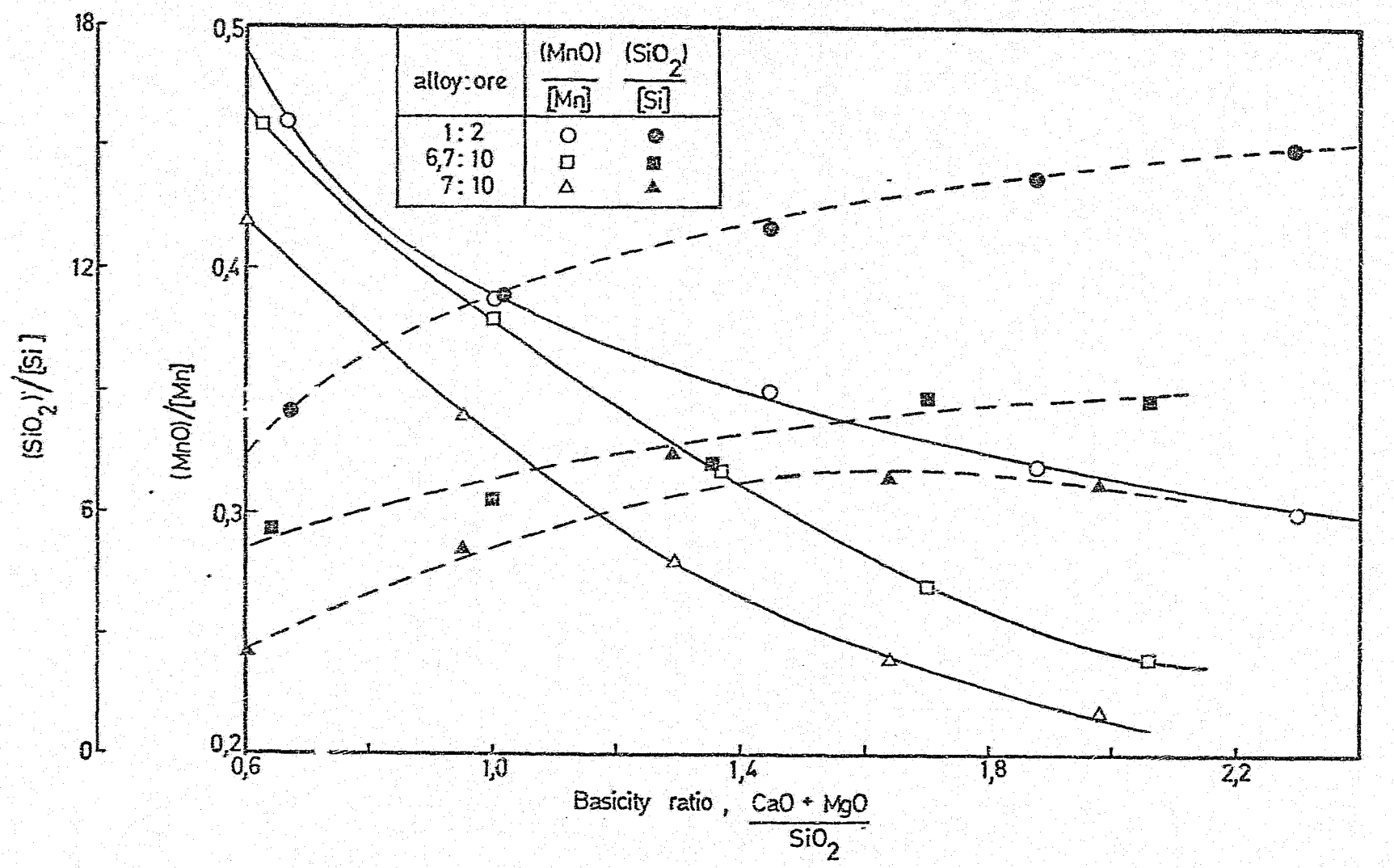


Figure 54. Effect of CaO additions and variations in the alloy-to-ore ratio on the manganese distribution and silicon distribution ratios.

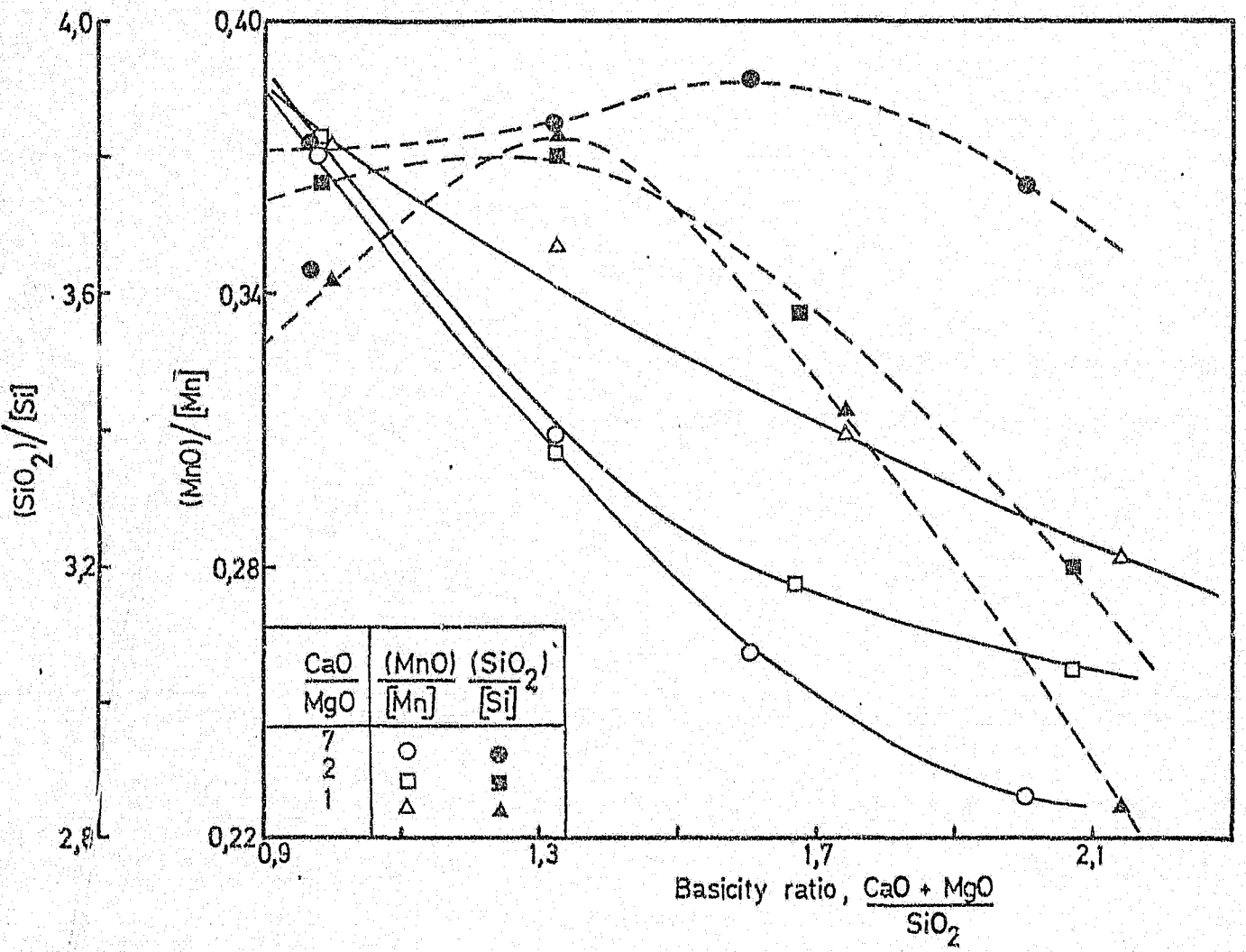


Figure 55. Effect of the replacement of CaO by MgO on the manganese distribution and silicon distribution ratios for a reaction with an alloy-to-ore ratio of 6, 7 to 10.

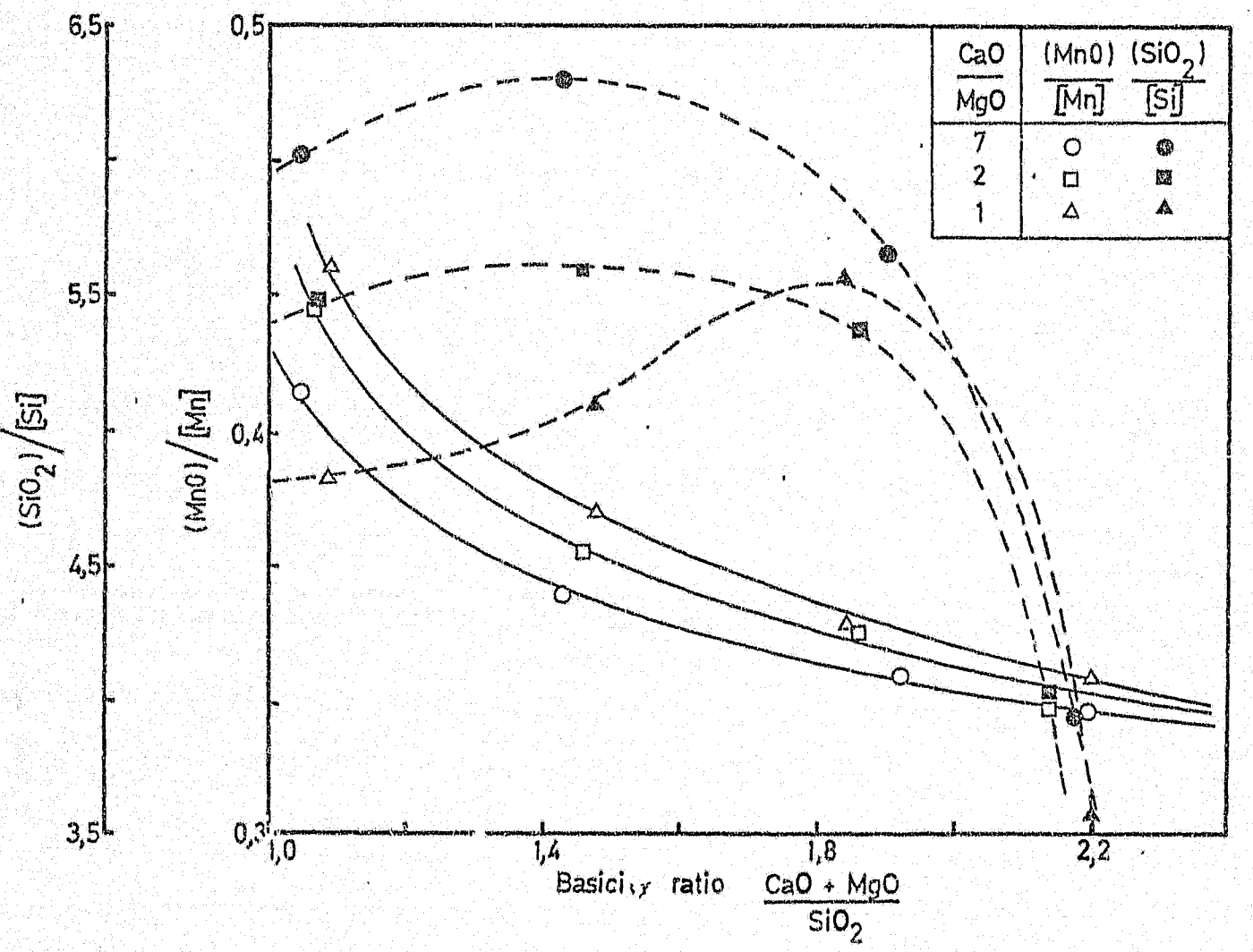


Figure 56. Effect of the replacement of CaO by MgO on the manganese distribution and silicon distribution ratios for a reaction with an alloy-to-ore ratio of 1 to 2.

that a high manganese distribution ratio is associated with a silicon distribution ratio whilst a low manganese distribution ratio is associated with a high silicon distribution ratio. These figures again illustrate the decrease in the value of the apparent equilibrium constant as the basicity ratio of the final slag is increased by CaO and / or MgO additions at a fixed alloy - to - ore ratio. High basicity ratios give low manganese distribution ratios although it is possible that this effect is caused by the decrease of the final MnO content of the slag owing to fluxing additions. Figure 54 shows that with increasing alloy - to - ore ratios, both the manganese and silicon distribution ratios decreased as the CaO flux additions were increased.

Tables 7 and 8 indicate that for a decrease in the CaO-to-MgO ratio there is an increase in the apparent equilibrium constant at any given flux addition. This increase suggests that a higher manganese distribution ratio is obtained although dilution of the MnO in the final slag does lower the manganese distribution ratio if large amounts of flux are used. Figure 55 shows that the manganese distribution ratio decreases for increasing CaO-to-MgO ratios with a stoichiometric amount of silicon in the reducing alloy.

As CaO is replaced by MgO, there is a decrease in the silicon distribution ratio for all the levels of flux additions investigated. As the amount of flux is increased the silicon distribution passes through a maximum which indicates that there is a particular range of basicities for efficient silicide refining. This final slag basicity range extends from a value of 1, 3 at low values for the CaO-to- MgO ratio to a value of 1, 6 at a high CaO -MgO ratio. No maximum was observed in the silicon distribution ratio when pure CaO was used as a flux and it can therefore be concluded that the MgO addition has a substantial effect on the silicon distribution ratio when large quantities of flux are used.

For large flux additions which reduced the CaO-to-MgO ratio there was a marked decrease in the silicon distribution ratio which may be attributed to an increasingly less favourable reaction. This

decrease is considered to be caused by an increase in the slag liquidus temperature and hence in slag viscosity as the MgO content of the slag is increased to above 10 mass per cent. No data was found for liquidus temperatures in the system $MnO-MgO-Al_2O_3-SiO_2$ except that of Warren et al[7] who used liquidus data for the system $CaO-MgO-Al_2O_3-SiO_2$[84] and showed that MnO in the quaternary system usually slightly lowers the liquidus temperatures by 30 to 40°C over the composition range investigated. Thus the MnO concentrations in final ferromanganese slags are expected to lower the temperatures of the liquidus surfaces in the $CaO-MgO-Al_2O_3-SiO_2$ system without affecting the overall configuration or relationship between the curvatures of these surfaces. The phase diagram shown in Figure 57 from Osborn et al[84] may therefore by taken as a reasonably good guide to the liquidus temperatures of slags on a recalculated basis where the slag MnO content is omitted and the concentrations of the other four components adjusted so that $CaO + MgO + SiO_2 + Al_2O_3$ = 100 per cent.

Figure 56 shows the relationships of manganese and silicon distribution ratios to the basicity ratio of the final ferromanganese slag for a 1 to 2 ratio of industrial ferromanganese - silicide to manganese ore. This ratio is used in industrial practice when the ferromanganese - silicide has a silicon content of approximately 22 mass per cent which is lowered to less than 1,5 mass per cent during refining. The manganese distribution ratio behaves similarly as for the additions of pure CaO or for the alloy-to-ore ratio of 6,7 to 10. The silicon distribution ratio also passes through a maximum which depends on the CaO-to-MgO ratio of the flux. These plots show that the optimum basicity ratio of the final slag lies between 1,4 to 1,8. Below a basicity of 1,4 refining is poor when a high magnesia flux is used and above a basicity of 1,8 there is a marked decrease in the silicon distribution ratio because of the formation of slag premelts which have high liquidus temperatures in excess of 1600°C for slag MgO contents greater than 12 mass per cent and hence higher viscosities of approximately 0,26 Ns/m^2 at 1500°C[85] compared to the usual values of approximately 0,15 Ns/m^2.

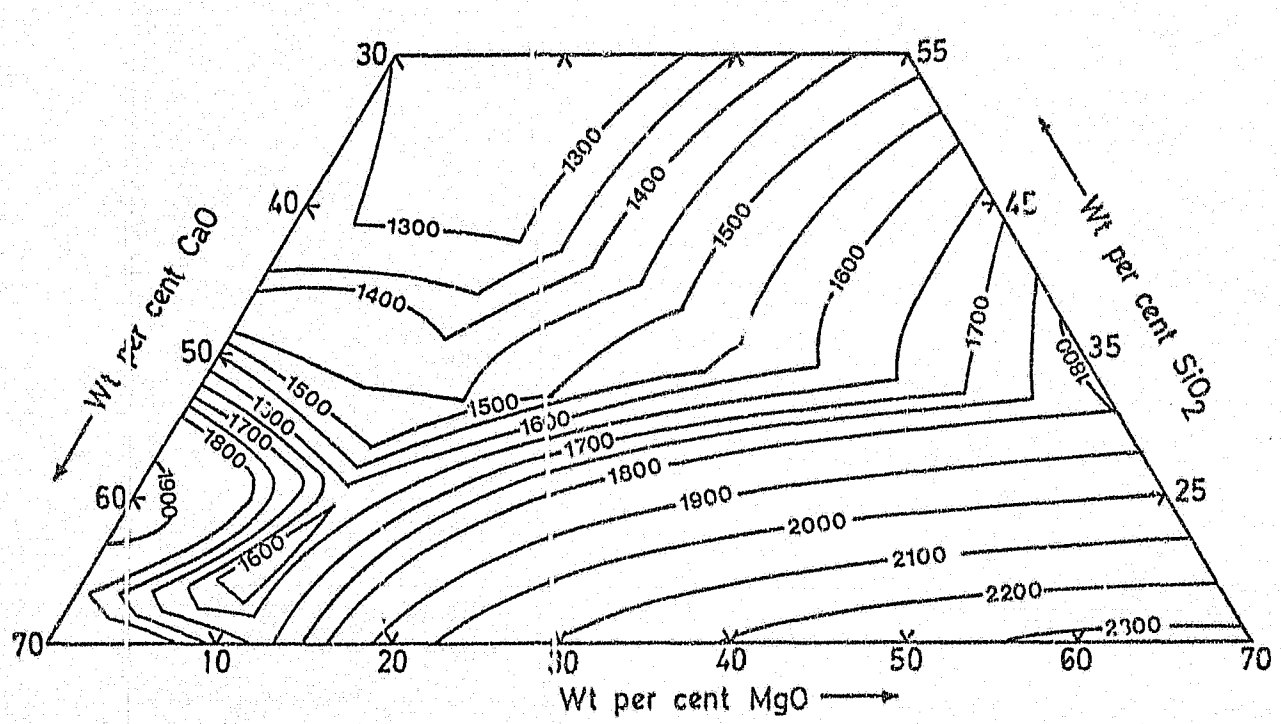


Figure 57. Liquidus diagram for the 15 mass per cent Al_2O_3 plane in the $CaO-MgO-Al_2O_3-SiO_2$ system after Osborn et al[134].

Comparison of Figures55 and 56 reveals that high alloy-to-ore ratios decrease the manganese distribution ratio and the silicon distribution ratio. Once again it must be stressed that the silicon distribution ratio is the most important factor in the production of a marketable ferromanganese alloy and this ratio should be maintained as high as possible.

Figures 54 to 55 show the various distribution ratios and apparent equilibrium conditions obtained for the complete sequence of fluxing additions studies. An additional aspect which was investigated was the reacti . between an unfluxed manganese ore and a range of ferromanganese - silicide reducing alloys containing up to 100 mass per cent silicon. Comparisons of silicon and manganese distribution ratios give information on the optimum silicon content for the reducing alloy to extract manganese from its ore and to produce a refined alloy. Although plant practice will almost certainly continue to be based on the use of an alloy containing about 20 per cent silicon, the laboratory study considered different alloy - silicon contents to suggest alternative possil . ies and to explore their thecretical implications.

The results of this study are shown in Table 9 and Figure 58 which are derived from Figure 44 in the results. The values of the apparent equilibrium constant show that a slight increase in K'_{Mn-Si} is observed as the reducing alloy silicon content is increased to 65 mass per cent. However the manganese distribution ratio does not inducate the extent of slag refining as the manganese content in the initial alloy was not kept constant (Table 5). The silicon distribution ratio decreases with increasing silicon content of the synthetic ferro - manganese. Hence a low silicon alloy should be utilized in the extraction process to produce the most refined alloy.

An unfluxed silicothermic reaction using a 22, 46 mass per cent silicon alloy at an alloy-to-ore ratio of 1 to 2 gives a silicon distribution ratio of approximately 9, as shown in Figure 54. To achieve this silicon distribution ratio when synthetic silicide alloys are used an alloy containing slightly in excess of 20 mass per cent silicon is necessary and this conclusion is in agreement with present industrial practice. Figure 58 shows the rapid decline in the

TABLE 9

ANALYSIS OF THE UNFLUXED REACTION WHEN SYNTHETIC FeMnSi ALLOYS WERE UTILIZED
ALLOY-TO-ORE RATIO 1 TO 2

Reducing Alloy Si Content (mass fraction)	Final compositions						Distribution ratios		Basicity ratio	Apparent equilibrium constant	
	Alloy (mass fraction)		Slag (mass fraction)				$\frac{(MnO)}{Mn}$	$\frac{(SiO)_2}{Si}$	$\frac{CaO + MgO}{SiO_2}$	$K = \frac{[Mn]^2(SiO_2)}{(MnO)^2[Si]}$	$K_1 = \frac{(MnO)\sqrt{[Si]}}{[Mn]}$
	Mn	Si	MnO	SiO_2	CaO	MgO					
0,15	0,809	0,006	0,500	0,197	0,139	0,031	0,618	32,80	0,86	85,9	0,048
0,20	0,802	0,024	0,440	0,242	0,146	0,032	0,549	10,08	0,74	33,8	0,085
0,30	0,767	0,076	0,350	0,307	0,156	0,034	0,456	4,04	0,62	19,4	0,126
0,40	0,721	0,131	0,293	0,355	0,161	0,036	0,406	2,71	0,55	17,5	0,147
0,50	0,683	0,182	0,203	0,420	0,173	0,038	0,297	2,31	0,50	26,1	0,127
0,65	0,603	0,255	0,154	0,438	0,171	0,038	0,255	1,72	0,48	26,5	0,128
0,80	0,423	0,423	0,266	0,373	0,165	0,037	0,629	0,90	0,54	2,23	0,409
0,90	0,322	0,585	0,344	0,314	0,157	0,035	1,068	0,54	0,61	0,47	0,817
1,00	0,215	0,635	0,391	0,280	0,151	0,034	1,819	0,44	0,66	0,13	1,400

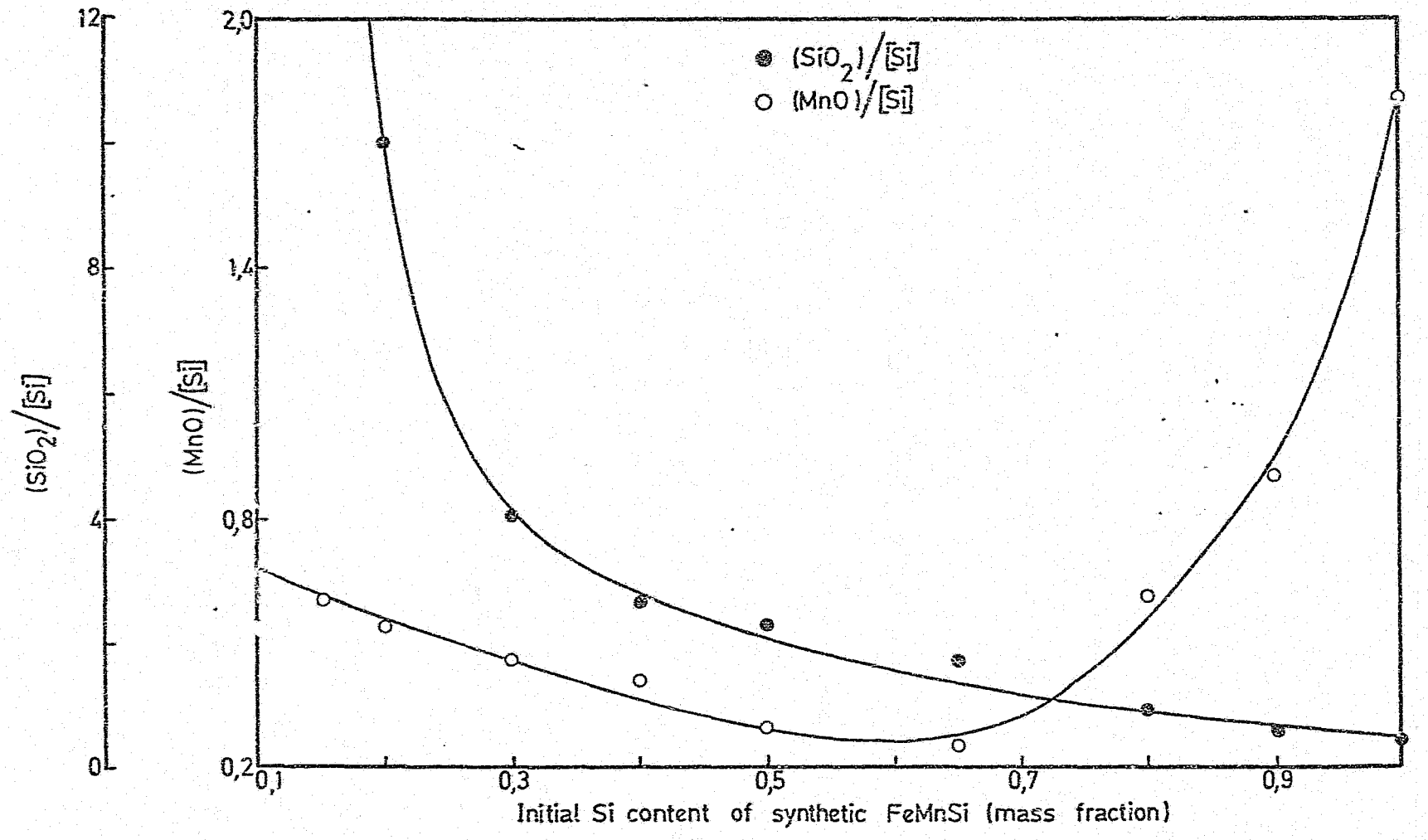


Figure 58. Variations in silicon and manganese distribution ratios for a non-fluxed reaction, alloy-to-ore ratio 1 to 2.

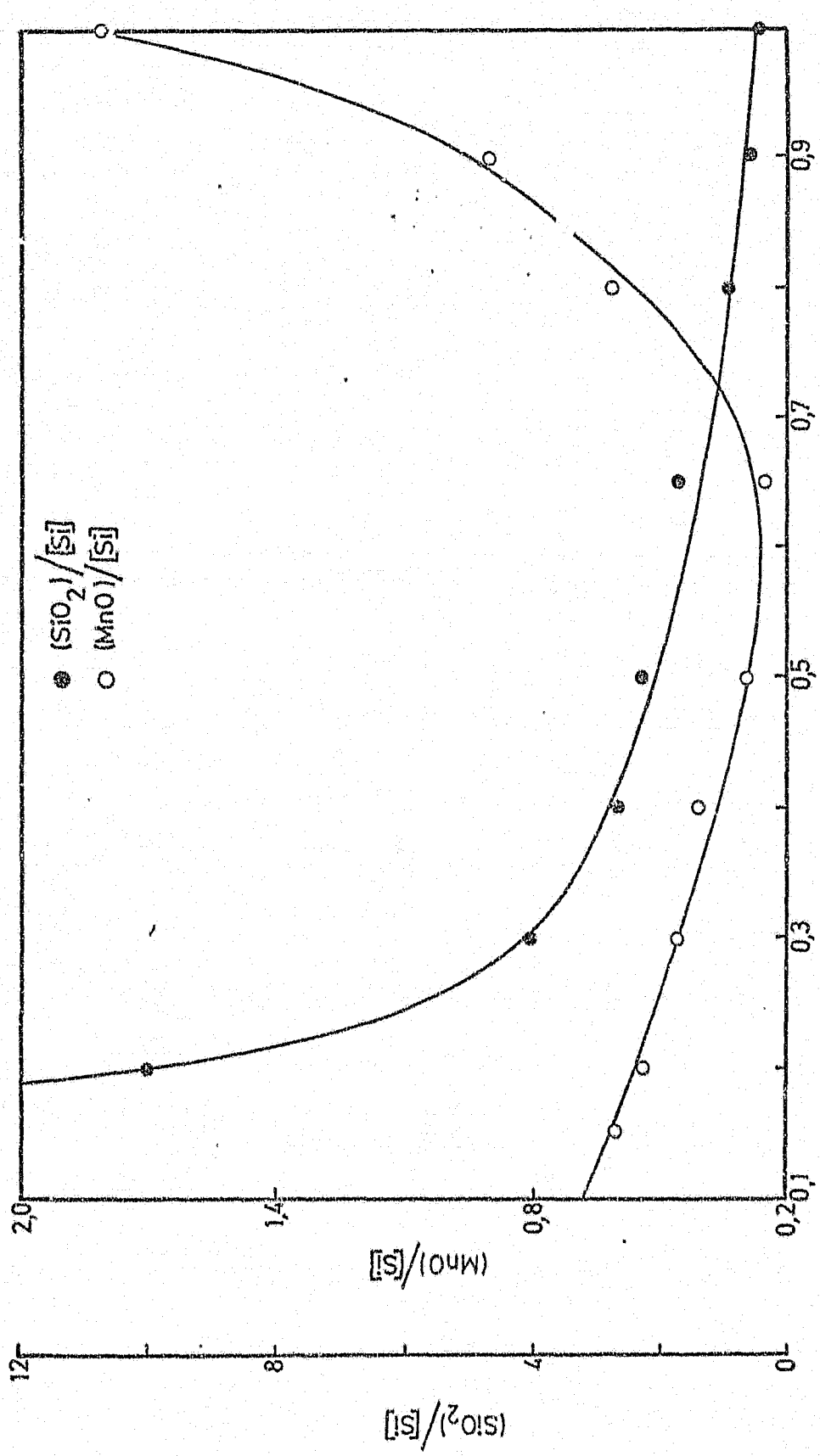


Figure 58. Variations in silicon and manganese distribution ratios for a non-fluxed reaction, alloy-to-ore ratio 1 to 2.

silicon distribution ratio as the silicon content of the reducing alloy is increased from 20 to 30 mass per cent. This shows that to achieve the same composition of the refined alloy as in industrial practice with a silicide alloy containing almost 30 mass per cent silicon, the ratio of the alloy to manganese ore premelt must be lowered.

6.1.3 Individual Fluxing Additions

6.1.3.1 No Flux Additions

Figure 36 shows the effect of two different alloy-to-ore ratios on manganese recoveries and alloy silicon content for non - fluxed reactions. For a particular alloy-to-ore ratio the resulting manganese and silicon distribution ratios depend on the fluxing components and the residual silicon content of the final alloy. To reduce all the manganese and iron oxides to manganese and iron respectively, the stoichiometric amount of silicon required is that present in the reducing alloy for an alloy-to-ore ratio of 6, 7 to 10. In industrial practice the alloy-to-ore ratio is 1 to 2 to ensure that the required low silicon levels will be obtained in the low-carbon ferromanganese.

The values of the apparent equilibrium constant in Table 6 confirm that with lower alloy-to-ore ratios the silicon content of the final alloy is lower. During the reduction reaction the activity of the MnO in the slag continually decreases because its concentration is reduced and, at the same time, the SiO_2 content of the slag is increased. The activity of the MnO is lowered still further because the Mn^{2+} ions in the slag become associated with polyanions made up of silicate anions SiO_4^{4-}, and thus the number of less strongly associated Mn^{2+} ions is decreased and their effective ionic fraction is lowered. As the silica activity is lowered, the silicon content of the ferromanganese - silicide reducing alloy is reduced until an apparent equilibrium is approached between the ferromanganese alloy and slag. Thus the activities of the reacting components and their dependence on slag and metal compositions must be studied to establish the nature of the final apparent equilibrium.

6.1.3.2 Alumina

The composition of the slag premelt will change because of dissolution of Al_2O_3 and it is necessary to discuss the effect of Al_2O_3 additions on the activity of MnO in the slag, the slag viscosity and the slag liquidus temperatures. It has already been maintained that, for a constant concentration of MnO in the slag, at a fixed value of the CaO-to-MgO ratio (4, 57) and at final values of basicity ratio over the range 0, 91 to 1, 66, there is very little change in the activity of MnO for changes in Al_2O_3 concentration from 10 to 20 mass per cent.

In addition, there is no appreciable change in the liquidus temperatures over this composition range for the quaternary system CaO-MgO-Al_2O_3-SiO_2 [84]. Similar trends occur when MnO is present in the system [7] although the slag liquidus temperatures are generally lowered.

Al_2O_3 has been shown by Woollacott et al [85] to have an insignificant effect on the slag viscosity. However it was shown that Al_2O_3 does affect the influence of the basic oxides on the viscosity. Woollacott et al found that for slags similar to those produced industrially in the low-carbon ferromanganese process (5 mass per cent MgO, 30 mass per cent MnO and CaO-to-MgO ratio of 1, 25) the slag viscosities measured at 1500°C, were 0, 11, 0, 15 and 0, 21 Ns/m^2 as the slag SiO_2 content increased from 27 to 32 and to 37 mole per cent respectively.

6.1.3.3 Lime

CaO is extensively utilized in the production of medium - and low- carbon ferromanganese to increase the activity coefficient of MnO and to reduce the slag viscosity by breaking up the silicate network. However excessive CaO markedly increases the slag liquidus temperatures and the slag viscosity is increased at any constant temperature with the consequence decrease in the rate of reduction. The effect of increasing CaO concentration on slag liquidus temperatures is illustrated by the quaternary system CaO-MgO-Al_2O_3-SiO_2 [84] (Figure 57) which shows that at slag MgO contents of less than 15 mass per cent, increasing the CaO content of the slag from 40 to 50 mass per cent increases the slag liquidus temperature from approximately 1300°C to 1450°C. Further increases in the CaO content in the slag, particularly at slag MgO contents of less than 10 mass per cent, result in sudden increases in the slag liquidus temperature to above 1600°C at CaO contents of 55 mass per cent.

The activity of MnO should be maintained as high as possible throughout the reduction reaction to efficiently extract manganese from the manganese ore premelt. During the reduction reaction, the MnO activity in the slag is continually decreased because of the presence in the slag of SiO_4^{4-} ions and the polyanions which are then associated with the Mn^{2+} and O^{2-} ions from the MnO.

CaO is the more basic oxide* and when it is introduced into the slag system it liberates more O^{2-} ions than MnO[86]. The SiO_4^{4-} ions and other polyanions associate preferentially with Ca^{2+} ions and the activity of the MnO in the slag is increased. An indication from studies on solid state systems that this preferential association may take place is the more negative standard free energies of formation of calcium ortho- and metasilicates compared to that of manganese metasilicate (Equations 3.12, 3.15 and 3.16).

The activity of a component in a multi-component system is related to its activity coefficient and mole fraction by the formula:

$$a_x = \gamma_x N_x \qquad 6.4$$

where a_x = activity of a component x for a particular standard state,
γ_x = activity coefficient of component x,
and N_x = mole fraction of component x.

Increases in the concentration of CaO in the slag increase the activity coefficient of MnO in the slag melt at any particular concentration of MnO. At the same time, increases in CaO additions to the slag containing MnO will decrease the mole fraction of MnO. Thus although CaO additions increase the activity coefficient of MnO, if excessive CaO additions are made the MnO activity may be lowered.

An unfluxed stoichiometric reduction reaction and a reaction fluxed with CaO are compared in Figure 37. For a reaction time of 15 minutes, the basicity ratio $(CaO+MgO)/SiO_2$ of an unfluxed Mamatwan ore melt is decreased from 3,5 to less than O,7. A slag basicity ratio of O,7 favours the association of Mn^{2+} ions with SiO_4^{4-} ions and other polyanions

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* It should be noted that the concept of slag basicity for reactions involving O^{2-} ions may require further examination in view of Wagner's recent critical analysis of this concept[87].

and leads to an eventual decrease in the rate of manganese recovery so that this recovery tends towards a constant value.

A CaO addition of 20 mass per cent permits the establishment of more favourable manganese and silicon distributions because of the increase in the MnO activity of the slag. For fluxing additions of 20 mass per cent, the slag basicity ratio $(CaO+MgO)/SiO_2$ changes from 7,4 to 1,45 as the reaction progresses. The final slag basicity value of 1,45 is in good agreement with the values of 1,3 to 1,5 in industrial practice[88]. The manganese recoveries of 40 per cent and alloy silicon contents of 1,0 mass per cent are also in good agreement with the values of 45 per cent and 0,8 mass per cent obtained industrially[88].

It has been suggested that in the melting of manganese ores, for subsequent reduction by ferromanganese - silicide, flux additions need not be made to the arc furnace immediately at the start of melting. A suggested procedure to minimize power costs and flux consumption would be to tap the furnace content of molten manganese ore into a reaction ladle, add reducing agent as solid ferromanganese - silicide and then add lime or dolomite in stages to complex the SiO_2 formed by the reduction reaction. The heat for the dissolution of the flux would be provided by the exothermic reduction reaction.

In the experimental study of the effect of stage-wise additions of CaO an unfluxed reaction with an alloy-to-ore ratio of 6,7 to 10 was permitted to continue for 5 minutes before flux was added. A temperature drop of approximately 20°C was recorded by the thermocouple at the top of the crucible wall, but the change in melt temperature would have been greater. Hence the CaO was not completely dissolved and the manganese recovery decreased compared to that for a lime - ore melt as shown in Figure 38. Consequently it is difficult to compare recoveries obtained from stage-wise CaO additions and lime - ore premelts in small scale experiments unless care is taken to preheat the CaO and thus eliminate cooling of the melt. In these small scale tests, the excess heat generated by the exothermic reduction is not sufficient to maintain the melt temperature at a fixed value if cold fluxing additions of the order of 20 mass per cent, are introduced to the reaction melt.

A similar effect might be observed on an industrial scale.

Figure 39 illustrates the effect of variations in CaO additions on the manganese recovery from the slag. For the reaction with the lowest alloy-to-ore ratio of 1 to 2 very low concentrations of silicon in the final alloy are obtained. From the data of Tolstoguzov[61], for the Fe-Mn-Si-C system, correspondingly low values for silicon activity can be expected. The manganese recovery plot relating to the low alloy-to-ore ratio practice passes through a maximum in recovery. For increasing additions of CaO the present investigation indicates that there must be an increase in the values of MnO activity in the slag below additions of 12 mass per cent. However at higher additions of CaO, although the activity coefficent of the MnO will be increased[7], lowering of the mole fraction becomes the predominent influence upon activity of MnO which is decreased. The activity of the silicon in the reducing alloy is low because of the low mole fraction of silicon and hence manganese recovery tends towards a constant value.

For higher alloy-to-ore ratios the activity of MnO will eventually decrease because of excessive CaO additions but the silicon activity in the alloy is sufficiently high to drive reaction 3.5 closer to equilibrium. Silicon activity coefficients are essentially constant in the Fe-Mn-Si-C system and values of $-\log_{10} \gamma_{Si}$ for alloys containing 1, 5 and 15 mass per cent silicon have been reported as 1, 55, 1, 82 and 1, 48 respectively[61]. Consequently activity values of silicon in the Fe-Mn-Si-C system vary almost directly with the silicon mole fraction.

Substantial increases in the slag liquidus temperatures do not occur at these high levels of CaO addition. This can be inferred from the quaternary system $CaO-MgO-Al_2O_3-SiO_2$ given in Figure 57. During the present investigation the CaO content of the final slag reached a maximum of 41 mass per cent. On a recalculated basis, when the slag MnO content is ignored, the maximum CaO content is approximately 47 mass per cent and the MgO content is approximately 7 mass per cent. The liquidus temperature corresponding to this slag composition in the quaternary $CaO-MgO-Al_2O_3-SiO_2$ system is 1500°C and with the introduction of MnO to the four component system slag liquidus temperatures will be lower.

6.1.3.4 Magnesia

MgO is similar to CaO in its effect on the activity of MnO in a manganese slag premelt. MgO is also a 'network modifier' as it reduces the average size of silicate polyanions in a slag. The Mg^{2+} ions preferentially associate with SiO_4^{4-} ions and increase the number of less strongly associated Mn^{2+} ions and as a result, the activity coefficient of the MnO is increased. Equations 3,12 to 3,17 show several standard free energies of formation in the solid state which indicate with the higher basicities of CaO and MgO than of MnO [86] that there should be a tendency for Ca^{2+} and Mg^{2+} ions to be preferentially associated with SiO_4^{4-} ions and other silicate polyanions such as $Si_2O_7^{6-}$ and $Si_3O_8^{10-}$. The number of less strongly associated Mn^{2+} ions in the slag will be increased with a corresponding increase in the activity coefficient of the MnO in the slag.

As CaO is replaced by MgO for a particular mass per cent of flux, there is an increase in the mole fraction of basic fluxing components due to the lower molecular weight of MgO compared to CaO. Hence the mole fraction of MnO in the slag is reduced although no dilution has occurred on a mass per cent basis. Thus although increased MgO additions increase the activity coefficient [7], the MnO activity does not necessarily increase. Warren et al [7] found that for any given Al_2O_3 and SiO_2 content the activity coefficient of MnO decreases as MgO replaces CaO on a mass per cent basis at high SiO_2 levels. In the more basic slags such as those encountered in the production of refined ferromanganese the activity coefficient of MnO increases initially from approximately 2,0 to 2,2 until the ratio of mass per cent CaO to mass per cent MgO reaches about 4. These authors, however, indicate that the increase in the activity of MnO is small in comparison with the effect of increasing basicity.

Increased concentrations of MgO from 5 to 10 mass per cent in slags associated with medium - and low - carbon ferromanganese production, lower slag viscosity from 0,23 to 0,21 Ns/m^2 at 1500°C. However, a limit to MgO additions is experienced at about 10 mass per cent and therefore the slag viscosity, measured at 1500°C, increases to

O, 26 Ns/m^2 for 18 mass per cent MgO[85].

The reduction in slag viscosity for increased MgO contents in the slag was shown by Woollacott et al[85] to be less when SiO_2 was replaced by Al_2O_3 at low concentrations of MnO in the slag. At high MnO concentrations as the slag Al_2O_3 content increases from 10 to 16 mass per cent, the slag viscosity increase with increased MgO content is less marked.

The present study considered the effect of replacing CaO by MgO to perhaps eventually replace CaO completely or partly with calcined dolomite. The use of dolomite, which is abundant in South Africa, could lead to vast savings in raw material costs if dolomite proved satisfactory in practice.

Figures 40 and 41 show results obtained in this investigation. The use of high alloy - to - ore ratios gives increased slag refining at any level of flux addition. However, with increased fluxing, a recovery maximum is achieved at alloy - to - ore ratios of 1 to 2 and 6, 7 to 10. The maximum in manganese recovery was also found to occur during the investigation of the effects of CaO additions on manganese distribution.

When MgO is used as a flux, manganese recovery was increased as shown in Figure 40 and this effect can be explained by an increase in the MnO activity of the slag[7]. For fluxing additions of more than 20 mass per cent MgO, it was not possible to melt the Mamatwan ore - MgO mix even at a temperature of 1550°C.

When MgO replaced CaO the manganese recovery always declined at a fixed flux addition. This is because the mole fraction of MnO was lowered as MgO was substituted for CaO since MgO has a lower molecular weight than CaO. As mentioned previously, Warren et al[7] have shown a slight increase in the activity coefficient of MnO as MgO replaces CaO, but as the mole fraction of MnO decreases with increasing MgO additions, it appears that the product of the MnO mole fraction and activity coefficient results in a decreasing activity of MnO with increasing MgO additions.

For large basic fluxing additions, increased liquidus temperatures and viscosities hinder the silicothermic reduction. For low alloy - to - ore ratios this effect was observed at all ratios of CaO - to - MgO and was also noted when CaO was used as the flux.

For the higher alloy - to - ore ratios of 6, 7 to 10 this decline in manganese recovery at particularly high flux additions became more obvious as the CaO - to - MgO ratio was lowered. The final slags produced by such additions contained MgO concentrations of between 12 and 19 mass per cent MgO and as previously stated these slags are associated with high slag liquidus temperatures and viscosities[7, 85].

Slags associated with low - and medium - carbon ferromanganese production will contain SiO_2 concentrations of approximately 35 mass per cent when recalculated on a mass per cent basis thus eliminating the MnO. Figure 57 shows that CaO can be used up to concentrations of 15 mass per cent at SiO_2 and Al_2O_3 concentrations of 35 and 15 mass per cent respectively. However, when the MgO concentration approaches 20 mass per cent the liquidus temperature increases to approximately 1500°C. Additions of CaO and /or MgO at this slag SiO_2 concentration give sudden increases in slag liquidus temperatures. Viscosity will increase with marked increases in the liquidus temperature because the super heat of the slag will be less at any particular temperature.

When a stoichiometric amount of ferromanganese - silicide is used and the fluxing addition is kept constant at 40 mass per cent, it should be possible to optimize the manganese recovery by varying the CaO - to - MgO ratio. This effect is shown in Figure 41 and the maximum manganese recovery was 58 per cent. The marked decrease in the manganese recovery is due to the increased liquidus temperature as may be shown by considering the quaternary CaO - MgO - Al_2O_3 - SiO_2 system. Variations in the CaO - to - MgO ratio from 7 to 1 at this flux addition level lead to increases in the final slag liquidus temperatures from 1500°C to 1750°C[84]. The MnO in the slag will lower these liquidus temperatures but only by a very small amount.

Vast reserves of dolomite exist in South Africa and if possible more use should be made of such deposits in the metallurgical industry. Dolomitic ore almost certainly can be blended with limestone or burnt lime to give

the flux composition necessary to ensure maximum manganese recovery and this effect has been demonstrated in the laboratory. However in industrial practice, the problems associated with higher slag liquidus temperatures and hence increased losses of manganese as manganese vapour and increased refractory wear, cannot be assessed at present.

In laboratory experiments, the calcined dolomite used was from the Transvaal Dolomite Series which is typical of dolomites in South Africa. The composition of this calcine is given in Table 3 and the ratio of the basic fluxing components CaO - to - MgO is 1,6. Figure 41 shows that manganese recoveries achieved with fluxing additions of 40 mass per cent of calcined dolomite are very near to the manganese recoveries obtained by varying the CaO - to - MgO ratio at constant flux addition of 40 mass per cent. Only a small increase in manganese recovery can be achieved over and above this value and this is obtained by increasing the CaO - to - MgO ratio from 1,6 to 3,0 at a level of flux addition of 40 mass per cent.

This small decrease in manganese recovery occurs over a wide range of fluxing additions when comparisons are made between the use of lime and calcined dolomite. This decrease is explained by the increased slag liquidus temperatures and consequent increases in viscosity as well as the decrease in the activity of MnO at a particular level of flux addition when calcined dolomite additions are compared with CaO additions. The increase in slag viscosity and decrease in the activity of MnO in the slag is caused by the introduction of the MgO in the dolomite. The decline in manganese recovery with the use of calcined dolomite is not severe and can be tolerated provided manganese losses to the slag can be offset by favourable costs of fluxing materials coupled with efficient operation of the arc furnace used for the premelt preparation.

When CaO and MgO are compared as fluxes it is apparent that CaO is the superior flux for the ranges of slag concentration encountered in the production of medium - and low - carbon ferromanganese. However, the use of MgO does not substantially decrease manganese recoveries

provided that not enough is used to dramatically increase the liquidus temperatures of the slag. Similar precautions should be taken when calcined dolomite is used as a flux addition.

6.1.4 Composition and Quantity of Reducing Alloy

Various grades of medium - and low - carbon ferromanganese are produced industrially. These grades are specified by their concentrations of contained manganese, carbon and silicon but generally these alloys contain in excess of 80 mass per cent manganese and less than 2 mass per cent silicon. As indicated in Section 6.1.3.1, the silicon and manganese distribution ratios during refining and specifications for the refined alloy limit variations in reducing alloy compositions and quantities.

Ferromanganese - silicide is the most commonly used reducing agent for the recovery of manganese from its ores. However, to reach the specified composition of the final alloy, industrial practice is to use alloy - to - ore ratios less than the stoichiometric requirements. Consequently, in a single stage process, large amounts of manganese are lost to the final slag which contains between 30 to 35 mass per cent MnO compared to its initial concentration of approximately 50 mass per cent MnO. When an industrial ferromanganese - silicide reducing alloy containing 22,46 mass per cent silicon is reacted with an unfluxed Mamatwan ore premelt, whose composition is given in Table 3, an alloy - to - ore ratio of 1 to 2 is required to simulate conditions of industrial practice whereas 6,7 to 10 corresponds to the stoichiometric quantity of silicon necessary for reaction.

Plant ferromanganese silicide alloys can contain up to 25 mass per cent silicon. The production of alloys with higher silicon contents produces slags containing high concentrations of SiO_2 and the submerged - arc furnaces must be operated at higher temperatures. However, this investigation made use of alloys with higher silicon contents than 25 mass per cent as well as alloys with aluminium additions in order to extend the study to a wider range of alloy compositions and to explore the practical possibilities and the theoretical implications of the use of these alloys.

6.1.4.1 Silicon Activities in Reducing Alloy

High activities of MnO in the slag and of silicon in the reducing alloy are necessary to maximise the transfer of manganese from the slag to the alloy. In a single - stage silicothermic reaction for the production of medium - and low - carbon ferromanganese, the permissible range of activities is limited by the necessity to obtain a refined ferro - manganese alloy which will meet market specifications.

Ferromanganese - silicide is the alloy used industrially for the silicothermic process although other alloys containing silicon could be utilized. Industrial ferromanganese - silicide contains carbon and very little data is available for activities in the ternary system Fe-Mn-Si and apparently none for the quaternary system Fe-Mn-Si-C.

Extensive work of the activity coefficients of silicon in the Fe-Si system has been reviewed by Darken[53] and Fruehan[89]. Activity coefficients for silicon in the ternary systems Fe-Si-C and Mn-Si-C have also been obtained at carbon saturation. Comparison of the binary Fe-Si and ternary Fe-Si-C systems indicates that at any silicon content the activity coefficient of silicon is increased when carbon is introduced into the binary system at 1500°. At the same temperature and silicon concentration the activity coefficient of silicon in carbon-saturated Mn-Si melts is much higher than that in carbon - saturated Fe-Si melts.

Three values have been published for the activity coefficient of silicon in the quaternary system Fe-Mn-Si-C[61]. When these values are compared with values obtained for equivalent silicon concentration in the Fe-Si system[53] it is noted that the respective activities are similar up to a silicon content of 15 mass per cent. Data relating to silicon activity coefficients at higher silicon content has not been published.

6.1.4.2 High Silicon Activities and Silicon Contents

Figures 43 to 48 show the effects on manganese extraction from a non-fluxed Mamatwan ore of variations in the alloy - to - ore ratio, silicon content of the reducing alloy and reducing alloy components. For a particular reducing alloy and an increased alloy - to -ore ratio, the manganese recovery will usually increase because a higher silicon activity is maintained throughout the reduction reaction. As the alloy mass is increased there will be less dilution of the alloy silicon content at any particular manganese recovery, and hence a smaller decrease in the silicon atomic fraction, so that a higher silicon activity will be maintained during the reaction. This is also the case for reactions in which the silicon content of the reducing alloy is increased at a fixed alloy - to - ore ratio.

Figures 44, 45, 46 and 48 show that increased manganese recoveries are not obtained when the reducing alloys contain high concentrations of silicon and high masses of silicon in relation to the mass of manganese in the slag. Similar behaviour is shown in Figure 49 when pure silicon is used as the reducing agent. The decline in manganese recovery after the maximum recovery in each figure is associated with poor separation of the slag and the alloy and with a tendency for the alloy to become more spherical as shown in Figure 50. This phenomenon cannot be ascribed to the activity of silicon in the Fe-Mn-Si-C system as all available literature, relating to associated alloys, show an increase in silicon activity coefficient with concentration.

The tendency of the reducing alloy to become spherical must be caused by variations in the interfacial tension between the slag and the alloy. The interfacial tension could be altered by the formation of a layer of solid silica on the surface of the alloy. This solid layer hinders the diffusion of reacting components across the slag-metal interface and reduces the rate of manganese transfer between the slag and the metal. When the reduction reactions were allowed to continue for periods of 45 minutes, the manganese recovery increased but at a slower rate. This decrease in reaction rate is consistent with

the hypothesis of the formation of a solid layer at the slag-metal interface which gradually dissolves in the slag so that the reaction continues at a reduced rate. Calculation of the conditions for the formation of a solid layer using the equation

$$[Si] + 2[O] = (SiO_2)_{(s)} \qquad 6.5$$

are not possible because of the lack of data on silicon activities in the alloy.

The decrease in manganese recovery after the maximum in the curves has been reached is due to the combined effects of the decrease in surface area between the alloy and the slag with the formation of an intermediate layer between the slag and the alloy. This effect occurs with increasing silicon contents in the alloy (Figure 44), increasing alloy-to-ore ratio (Figure45), increasing silicon content of ferrosilicon (Figure 46), increasing alloy-to-ore ratio of ferrosilicon (Figure48) and increasing mass of ferrosilicon (Figure 49).

Although the effect requires much more detailed examination as is indicated in Section 6.3 on future work, it is possible to make the following general comments. There are two effects demonstrated by Figures 44, 45, 46, 48 and 49. These are that the abrupt decrease in manganese recovery is associated with the mass of the alloy through an increase in the alloy-to-ore ratio (Figures 45, 48 and 49) or with an increase in the activity of silicon in a constant mass of alloy (Figures 44 and 46).

If a solid layer does form on the surface of the alloy, the effect of increased alloy masses could well be to make this solid layer formation more likely, because the stirring in the larger alloy mass may be reduced. If the stirring in the alloy is reduced then the flux of silicon from the bulk of the alloy to the slag-metal interface will decrease and oxygen will diffuse into the bulk of the alloy to react and form solid silica. The rate of formation of solid silica is greater than its rate of dissolution in the slag.

If the activity of silicon in the alloy is increased, then reaction 6.5 may proceed so quickly that it is not possible for the solid silica to be

immediately dissolved in the slag.

These comments are highly speculative and the inability to explain the observed phenomenon in a more quantitative manner means that further investigation is warranted.

Figures 47 and 48 confirm that ferrosilicon a superior reducing alloy to ferromanganese - silicide because of the higher activity coefficient of silicon in the ferrosilicon alloy at any silicon level. Both the ferrosilicon and ferromanganese - silicide alloys utilized in this investigation are industrial alloys and are saturated with carbon. The solubility of carbon in ferrosilicon alloys decreases as manganese replaces iron[58]. This dissolved carbon substantially increases the silicon activity coefficient and this can be shown from an analysis of previously published data where the activity coefficient of silicon in the binary Fe-Si system varies from O, OO2 to O, O2 over the range of silicon mole fractions from O to O, 3 while the corresponding activity coefficient values for the ternary Fe-Si-C system are O, O112 and O, O634[53, 54]. However, comparable data for the Fe-Mn-Si-C system are not available but the present investigation indicates that lower values of the activity coefficient will exist in the quaternary Fe-Mn-Si-C system.

6.1.4.3 Aluminium Content of Alloy

Aluminium could be used as a reducing agent together with ferromanganese - silicide during the production of medium - and low - carbon ferromanganese without substantial increases to production costs, provided small quantities of aluminium give satisfactory increases in manganese yields. To assess the effects of aluminium additions, experiments were carried out using increased aluminium additions to a reducing alloy which always contained the same mass of silicon. Figure 51 shows that the manganese recovery increased dramatically up to aluminium additions of 20 mass per cent. With increased aluminium additions, the final aluminium concentration was below O, 3 mass per cent while the final alloy silicon concentration increased sufficiently to produce a poor quality ferromanganese. This effect is explained by the competition between the more thermodynamically favourable aluminothermic reaction. As a result aluminium largely replaces silicon as the reducing agent . The aluminothermic

reduction reaction and silicothermic reduction reactions can be represented by equations 6.5 and 3.5 respectively.

$$MnO + .2/3Al = Mn + 1/3Al_2O_3 \qquad 6.6$$
$$\Delta G^\circ = -166000 + 20,15\ T \text{ Joules } (1517 \text{ to } 1973\ ^\circ K)$$

The standard free energy of formation of one mole of liquid manganese by the silicothermic process is $\Delta G^\circ = -65600 + 10,85\ T$ Joules (1686 to 1973 $^\circ K$). Thus at 1500$^\circ C$ the aluminotheric reaction has a negative standard free energy of formation of 130300 Joules relative to one mole of liquid manganese, compared to the silicothermic reduction reaction value of 46350 Joules.

The liquidus temperature diagrams of Osborn et al[84] reveal that no appreciable increases in slag liquidus temperatures occur in slags of the $CaO-MgO-Al_2O_3-SiO_2$ system even at Al_2O_3 contents of 35 mass per cent, when the slag MgO content is below 5 mass per cent.

Figure 51 suggests that approximately 5 mass per cent or less of aluminium could be used to achieve higher manganese recoveries without markedly increasing the silicon content of the alloy.

6.1.5 Stirring of Reacting Melt

The majority of the reduction reactions performed during this study were conducted without stirring. Stirring of the reacting melt was carried out to achieve enhanced manganese recoveries more quickly and to determine the rate controlling step in the reaction even though the experimental procedure made it impossible to carry out a detailed kinetic analysis.

Stirring decreased the manganese recoveries when compared to the unstirred reaction. This result conflicts with that of Daines and Pehlke[74] who showed that for alloys containing low silicon concentrations, there is a marked increase in the rate of manganese mass transfer between the slag and the alloy. This effect is shown in Figure 25.

In the present investigation, manganese recovery decreased with increased stirring time . In addition manganese recoveries were

generally lower with stirring, over the entire range of silicon concentrations in the reducing alloy as shown in Figures 52 and 53. Only the slag phase was stirred and in these two series of experiments, the discrepancy in manganese recoveries between the unstirred and stirred reactions was not caused by physical entrapment of the alloy within the slag phase.

The decrease in manganese recovery with stirring is believed to be due to a combination of two factors. When the silicothermic reaction begins the melt temperature is suddenly raised by approximately 100°C (Figure 34). Although the alumina stirring rod had been preheated to the initial furnace temperature prior to the beginning of the reaction, a considerable temperature difference will exist between the rod and the melt. If this stirring rod is introduced into the reaction melt, heat is removed from the slag-alloy system partly by the rod. In addition, stirring of the reacting melt after the initial violent reaction has subsided, ensures more rapid dissipation of the heat and faster cooling of the alloy and slag. Hence stirring enables the manganese and silicon distributions to revert more rapidly to values consistent with the furnace temperature as well as the final alloy and slag compositions.

6.2 Comparison of Certain Aspects of this Study with Previous Work

Slag - metal relationships associated with the production of medium - and low - carbon ferromanganese have been investigated by Barcza[67]. The studies on the reactions of the slag phase involved examination of the behaviour of ore and fluxes on heating, as well as the behaviour of these components during oxidation and reduction. A synthetic standard slag of 55 mass per cent MnO_2, 35 mass per cent CaO, 5 mass per cent MgO and 5 mass per cent SiO_2 was used. The composition of this slag was based on the chemical analysis of Mamatwan ore and limestone. The reducing agent was a plant ferromanganese - silicide alloy containing 11,1 mass per cent Fe, 65,6 mass per cent Mn, 22,4 mass per cent Si and O,46 mass per cent C. Barcza used synthetic premelts and thus it is possible to compare reactions between an alloy and the synthetic slag to reactions between an alloy and a premelt from naturally occurring Mamatwan ore.

Typical results for the variation in manganese recovery with time agreed with the present study in that the reaction was rapid, appeared to reach an apparent equilibrium within a few minutes and the initial reaction temperature did not affect the manganese recovery. However recoveries using the synthetic premelts were consistently much higher than for Mamatwan ore premelts. The Mamatwan ore does contain a small amount of iron oxide which would require silicide for its reduction but the difference in manganese recovery between synthetic and natural premelts are substantial and cannot be explained in this way. The difference in manganese recovery is possibly due to differences in the oxidation state of the manganese when synthetic and natural occurring slags are compared. In natural manganese slags the manganese is associated with oxygen as Mn_3O_4 when subjected to oxygen partial pressures and temperatures which are inherent in the reaction reaction system.

The use of CaO as a flux had a much greater influence on manganese recoveries for experiments with synthetic melts. Manganese recoveries increased from 32 to nearly 60 mass per cent as the CaO content in the premelt was increased from 0 to 30 mass per cent. Additions

of more than 30 per cent CaO decreased manganese recovery. This decline in recovery with increased CaO addition was also observed in the work in this thesis when Mamatwan ore was used and the alloy-to-ore ratio was 1 to 2. The drop in recovery occurred at a CaO addition of 15 mass per cent or approximately 27 mass per cent of contained CaO.

In experiments involving the replacement of CaO by MgO at a flux addition level of 40 mass per cent the present study shows that manganese recovery decreases at CaO-to-MgO ratios of less than 3. Barcza's work showed a drop in manganese recovery at CaO-to-MgO ratios of less than 1 for alloy-to-ore ratios of 1 to 2. An increase in manganese recovery was obtained as the CaO-to-MgO ratio dropped to 1.

In both studies, increasing the alloy-to-ore ratio allowed the reduction reaction to proceed further towards completion when plant ferromanganese - silicide was used. Variations of the silicon content of the reducing silicide alloys produced similar decreases in manganese recoveries after a maximum value. Barcza[67] considered the reduction of synthetic premelts by pure silicon and ferromanganese - silicide alloys containing 10, 22, 5 and 30 mass per centsilicon.

The present study and that of Barcza show the same general trends for all variations in fluxing and silicide additions. The single-stage reactions reveal that even for the optimum conditions, only moderate manganese recoveries are possible because of the establishment of certain silicon and manganese distributions. Further, for maximum manganese recovery, the silicon content of the alloy is too high for the usual grades of medium - and low - carbon ferromanganese. Both multi-stage or countercurrent reactions between slag and alloy are possible processes by which manganese recoveries can be improved. The simplest example of a multi-stage process[67] is illustrated in Figure 59.

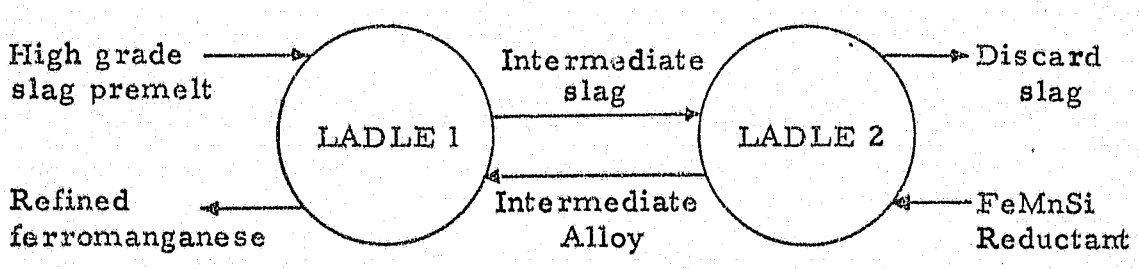


Figure 59. A two-stage refining process after Barcza[67].

By reacting the correct slag and alloy compositions at specified alloy-to-ore ratios it is possible to produce a highly refined alloy and a discard slag with a low MnO contents in a two-stage refining process. Ladle 2 would be used primarily for refining of alloy whilst the reaction in Ladle 1 would be to lower the final MnO content of the slag[67].

In a countercurrent reaction, a slag and a reducing alloy are allowed to react in a single vessel whilst the slag and the alloy flow in opposite directions to each other. This ensures that a slag with a high manganese content will contact an alloy with a low silicon content whilst a slag with a low manganese content will contact an alloy with a high silicon content. Thus optimum manganese and silicon distribution ratios will be obtained.

Countercurrent reactions have the advantage that intermediate slag and alloy products need not be handled. This process could be adapted to normal plant practice far more easily than a multi-stage process which would envolve considerable difficulties in synchronising tapping and handling procedures in conventional ferro - alloy plants.

6.3 Future Work

1. More detailed information is required on the activities of components in both the alloy and slag phases associated with the production of medium - and low - carbon ferromanganese to assist in the interpretation of the mechanisms and rates of reduction of manganese from fluxed and non-fluxed manganese ores.

2. The diffusion of components, particularly in the alloy phase, could have a major influence on the reaction rates. Diffusivities of both manganese and silicon should be measured over the entire composition range of ferromanganese - silicide alloys used in ferromanganese production.

3. Improvements to existing practices for the production of ferromanganese that require investigation are the agitation of reacting melts by gases and the use of a molten reducing alloy.

4. The measurement of the heat of reactions for the reduction of manganese oxides from slags by alloys with different silicon contents should be attempted. This data would assist in the development of heat balances for multi-stage and countercurrent processes.

5. One aspect of the present investigation considered the effect of increasing silicon content of the reducing alloy on the recovery of manganese from the slag. Particular attention should be given to the unfluxed reaction series shown in Figure 44. An extension of this work would invdve fluxing this reaction series with the aim of optimizing the fluxing additions for this range of silicon contents. The proposed research could show an appreciable increase in manganese recovery at any silicon concentration. As first pointed out by Barcza[67], this would have significant effects on industrial practises if a two-stage refining process were used. The primary stage would concentrate on extracting manganese from the manganese-rich melt without much attention to alloy refining. The second stage would then refine the intermediate silicide alloy using a high-grade slag which could be recycled to the primary stage as shown in Figure 59.

6. Further research is required on the utilization of reducing alloys

containing high silicon concentrations. Thus a mechanism might be proposed for the decline in manganese recovery at higher alloy silicon contents and the associated sudden change in the shape of the alloy.

7. CONCLUSIONS

1. Because of the exothermic nature of the reactions, there appeared be no substantial increase in manganese recovery in the alloy phase for increases in the reaction temperature from 1450°C to 1600°C.

2. For an alloy-to-ore ratio of 1 to 2 and CaO additions of 20 mass per cent, the manganese recovery increased by 5 mass per cent compared to the non-fluxed process.

3. When fluxing additions of CaO were increased to 40 mass per cent there was an apparent increase in the MnO activity of the slag. This activity appeared to decrease subsequently due to dilution effects or increased slag liquidus temperatures caused by larger additions of CaO.

4. Lower manganese recoveries were obtained for stage-wise additions of CaO compared to reactions in which CaO had been incorporated into the premelt.

5. Manganese recovery declined as the CaO-to-MgO ratio decreased for any particular percentage of basic fluxing additions.

6. The replacement of CaO by MgO at high levels of flux additions gave marked increases in slag liquidus temperatures and corresponding decreases in manganese recovery.

7. The use of calcined dolomite as a flux did not appreciably lower the manganese recovery obtained as compared with the use of CaO as the fluxing component.

8. As the silicon contents of the alloys and the alloy-to-ore ratio were increased, the recovery of manganese passed through a maximum and subsequently decreased. This decrease is associated with a change in shape of the alloy layer which becomes spherical and may be caused by the formation of a solid layer of reaction product on the alloy surface.

9. Ferrosilicon was a better reducing agent than ferromanganese-silicide for a fixed silicon concentration because of its higher silicon activity.

10. Aluminium improved manganese recoveries from a manganese-bearing slag because the aluminothermic reduction reaction occurred preferentially to the silicothermic reaction and the apparent equilibrium was reached at lower MnO contents in the slag.

11. Stirring of the reacting melt decreased manganese recovery from the slag. This was probably due to more rapid dissipation of the heat of the reaction leading to lower melt temperatures which are associated with lower manganese recoveries.

APPENDIX 1

Prediction of Manganese Recoveries from Alloy Mass Gains for the Reduction of Manganese - Containing Slags by Silicon

Extensive use is made of the silicothermic reduction of manganese - containing slags in the production of medium - and low - carbon ferro-manganese alloys. In this mass transfer process, the mass of the reducing alloy increases due to the mass of the iron and manganese extracted from the slag premelt whilst the slag basicity decreases because of the formation of silica according to reaction 3.5. It has been shown that the FeO in the slag is reduced by carbon to very low concentrations before reduction of MnO takes place[61, 62]. During the silicothermic reduction of Mamatwan ore it was also noted that the FeO concentrations in the slag were rapidly reduced to low levels whilst MnO reduction occured over a longer period. This is shown in Table 10 and confirmed by Figure 23 from which it may be concluded that the reduction of FeO by silicon is thermodynamically more favourable than the reduction of MnO by silicon.

It is therefore possible to correlate mass changes of the alloy with the manganese recoveries from the slag premelts. Manganese recovery is defined as the manganese transferred from the premelted ore to the alloy as a function of the total manganese originally présent in the premelted ore. Manganese recoveries can therefore be calculated from a combination of the alloy mass gain and alloy analytical results before and after reaction, or simply from the equation derived from theoretical considerations using the change in mass of the alloy.

The following derivation for manganese recovery is valid once the FeO concentration of the slag has been reduced to its equilibrium value with metallic manganese (about 0,1 mass per cent)

(i) Alloy Mass Loss

Losses in alloy mass initially occur by the reduction of Fe_2O_3

TABLE 10

TRANSFER OF MANGANESE AND IRON FROM SLAG TO ALLOY DURING UNFLUXED REACTIONS

Plant alloy-to-ore ratio 1 to 2

Temp. °C	Time min	Alloy		Slag		Recovery	
		Mn %	Fe %	Mn %	Fe %	Mn %	Fe %
1500	0,0	65,20	11,05	46,20	16,77	0,00	0,00
	0,25	70,04	12,43	42,18	4,47	10,07	25,48
	0,5	76,90	16,35	30,65	0,21	32,90	91,90
	1,0	76,87	16,63	30,96	0,14	32,88	97,28
	2,0	77,58	16,53	31,35	0,28	33,39	94,02
	3,0	77,01	16,52	29,72	0,07	34,95	98,34
	4,0	77,54	16,04	28,33	0,07	35,45	91,17
	5,0	76,73	16,79	30,65	0,07	36,07	94,96
	10,0	77,18	16,46	29,41	0,07	36,16	93,78
	15,0	77,93	16,27	27,79	0,07	35,99	94,11
1550	0,0	65,20	11,05	46,20	16,77	0,00	0,00
	0,25	76,11	14,80	29,88	1,68	7,94	85,50
	0,5	76,98	16,08	30,26	0,49	32,28	87,58
	1,0	76,44	16,46	28,72	0,21	32,28	94,02
	2,0	77,15	16,62	29,18	0,14	34,40	98,62
	3,0	77,30	16,48	29,18	0,14	35,14	97,70
	4,0	77,05	16,52	28,48	0,14	34,82	98,62
	5,0	76,59	16,51	28,19	0,14	34,29	98,62
	10,0	76,77	16,48	28,87	0,14	34,19	97,78
	15,00	76,84	16,43	26,47	0,22	33,76	96,86

and Mn_3O_4 to FeO and MnO without the transfer of iron or manganese from the slag to the alloy. From the ore analyses and the use of a standard ore mass of 25 g., the mass of silicon used for each stage of the reduction can be calculated from atomic weight data.

An ore premelt sample contains 1, 55 g Fe_2O_3 and 13, 116 g . Mn_3O_4. The reduction reactions are:

(a) $2Fe_2O_3 + Si = 4FeO + SiO_2$ ..... (1)

The silicon used to reduce 1, 55 g. Mn_3O_4 to FeO = O ,137 g.

(b) $2Mn_3O_4 + Si = 6MnO + SiO_2$ ..... (2)

The silicon used to reduce 13, 116 g. Mn_3O_4 to MnO = O, 805 g.
Silicon used in the formation of FeO and MnO = O, 942.

(ii) Alloy Mass Gain

Alloy mass gains occur because of the overall transfer of iron and manganese from the slag to the alloy. Alloy mass losses occur because silicon is transferred from the alloy to the slag.

(a) Mass gain due to the reduction of FeO

$2FeO + Si = 2Fe + SiO_2$ ..... (3)

From a 25 g ore sample the transfer of iron from the slag to the alloy is 1, O62 g. leaving a residual content of O, O9 per cent FeO in the final slag. This residual FeO analysis is in good agreement with the results of Boronenkov[63].

The alloy mass gain related to reaction (3) for the transfer of iron is:

$$1,062 \times \frac{83,61}{111,7} = O,795 \text{ g}$$

At the start of manganese recovery, the alloy mass loss is therefore:

$$O,942 - O,795 = O;147g \quad \ldots\ldots\ldots (4)$$

(b) Mass gain due to the reduction of MnO

$2MnO + Si = 2Mn + SiO_2$ ..... (5)

If ΔM^{A}_{obs} = observed mass gain of the alloy then

$(0,147 + \Delta M^{A}_{obs})$ = mass gain due to manganese recovery.

Considering equation (4) and the relevant atomic weights, the mass gain of manganese is given by:

$$(0,147 + \Delta M^{A}_{obs}) \times \frac{109,88}{81,79} \text{ g.}$$

As the ore premelt originally contained 9,4475 g. of manganese the manganese recovery can be given as

$$\text{Manganese recovery} = 1,3434 \frac{(0,147 + \Delta M^{A}_{obs})}{9,4475} \times 100\%$$

$$= 14,22 (0,147 + \Delta M^{A}_{obs}) \%$$

Comparisons of the recoveries achieved using this equation, with recoveries determined from mass gains and analyses, are in good agreement. The theoretically predicted recoveries are generally within one per cent of the recoveries derived from analytical results over a range of manganese recoveries from 10 to 40 per cent as shown in Table II. This result is within the limits of the experimental error when one considers the errors in measurement of the alloy, mass, alloy sampling and analytical techniques.

TABLE 11

PREDICTED AND ANALYTICAL-BASED MANGANESE RECOVERY COMPARISONS ASSOCIATED WITH UNFLUXED SILICOTHERMIC REACTIONS

Plant alloy-to-ore ratio 1 to 2

Temp. °C	Time min	Manganese recovery based on: Analysis %	Prediction %
1500	0,25	10,33	10,07
	0,5	33,16	32,90
	1,0	33,63	32,88
	2,0	33,65	33,39
	3,0	35,22	34,95
	4,0	35,77	35,44
	5,0	35,70	36,07
	10,0	32,60	36,16
	15,0	35,10	35,99
1550	0,25	28,22	27,94
	0,5	32,56	32,28
	1,0	32,54	32,28
	2,0	34,72	34,40
	3,0	35,37	35,14
	4,0	35,01	34,82
	5,0	34,88	34,29
	10,0	34,49	34,19
	15,0	34,00	33,76

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